Supporting Information for

“Fe\textsuperscript{0} nanoparticles remain mobile in porous media after aging due to slow desorption of polymeric surface modifiers”

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Three pages

\textbf{Figure S1.} Electrophoretic mobility of bare and polyelectrolyte modified nZVI as a function of pH and in the presence of excess polyelectrolyte in solution.

\textbf{Figure S2.} Grain size distribution of silica sand used in column experiments.
FIGURE S1. Electrophoretic mobility of bare nZVI (◇) and nZVI modified by PAP10K (●), CMC700K (■) and PSS1M (▲) as a function of pH, in the presence of excess polyelectrolyte in solution, after 5 days of equilibration. nZVI concentration was 15 mg/L and ionic strength was controlled at 5 mM NaHCO₃.
The isoelectric point decreased to pH ~2.2 for fresh PAP-modified nZVI (Figure S1) and to pH ~2.0 for fresh CMC-modified nZVI when excess polymer exists in the solution during pH adjustment. This is consistent with other studies of carboxyl-modified iron oxide nanoparticles in aqueous suspension. (1). For PSS-modified nZVI, the nanoparticles remained negatively charged over the entire pH range evaluated, consistent with the pH-independent ionization of strong polyelectrolytes. Note that the EPM is more negative at low pH when polyelectrolyte remains in solution during the EPM measurements, compared to when the pH was adjusted after washing excess polyelectrolyte out of the system. When excess polyelectrolyte is present at low pH, additional adsorption to the more positively charged surface can occur, thereby increasing the total charge due to adsorbed polyelectrolytes. Excess polymer in the solution is the best-case scenario that nZVI can have the highest mobility and might be a good way to further improve the colloidal stability and transport but this was not explored here.

The shift in the pH_{iep} for the bare nZVI from pH 6.3 to 3.7 over 16 weeks is noteworthy. The change is likely related to oxidation of the magnetite shell to maghemite (2). The initial washing step decreased the pH_{iep} of bare particles from pH_{iep} 6.3 to pH_{iep} ~4.4, presumably due to partial oxidation of the particles. Deoxygenating the washing solution did not significantly change the result (pH_{iep} decreased from 6.3 to ~4.7). Using very fresh nZVI containing a high initial Fe^0 content (~60 %) yielded pH_{iep} ~6 in both unpurged and deoxygenated cases, suggesting that the change of the surface charge is more sensitive to the initial Fe^0 content than to dissolved oxygen. The higher Fe^0 content likely mitigates the oxidation of magnetite.
Figure S2. Grain size distribution of silica sand used in column experiments. AFS Grain number is reported as 35 and effective grain size reported as 0.3mm by manufacturer Agsco Corp., Wheeling, IL.

Literature cited
