

SERDP Project ER-1487
Quarterly Progress Report-GT Contribution
For the period
15 July 2009

Task II: Transport and reaction of nanoscale iron in a representative porous medium

Milestone 2.4. Comparison of chlorinated ethene reactivity with different types of nZVI (in progress, completed 6/2009)

During this reporting period additional column experiments were conducted to evaluate the effect of increasing the amount of nanoscale zero valence iron (nZVI) delivered to a dense non-aqueous phase liquid (DNAPL) source zone in an effort to improve overall reactivity. Specifically, we wanted to determine if increasing the molar ratio of iron to tetrachloroethene (Fe:PCE) by a factor of 10 (from 0.5 and 5.0) would result in a proportional increase in the amount of PCE-DNAPL that would react to form daughter products (e.g., ethene). As noted in previous progress reports, Toda Americas Inc. no longer supplies small quantities of reactive iron nanoparticles (RNIP), and therefore, we are currently using other commercial nZVI vendors. For the experiments described herein, nZVI was obtained from a vendor located in the Czech Republic, and this form of nanoscale iron will be referred to as CR-nZVI.

To facilitate delivery to the PCE-DNAPL source zone, surface-modified CR-nZVI was prepared by mixing either 10 g/L or 40 g/L of commercial CR-nZVI with Tween 80 surfactant. One dimensional (1D) column (15 cm length by 2.5 cm inside diameter) experiments were conducted to evaluate both the delivery and reactivity of CR-nZVI in the presence of residual PCE-DNAPL. To establish a uniform residual saturation of PCE-DNAPL, neat PCE was introduced in an up-flow mode into a vertically-oriented column packed with water-saturated 20-30 mesh sand until approximately 80 percent of the pore volume contained PCE-DNAPL. Four pore volumes of de-ionized (DI) water containing 10 mM NaHCO_3 as a background electrolyte were then introduced into the column in a down-flow mode to displace the mobile fraction of PCE-DNAPL, leaving behind residual PCE-DNAPL at saturations that ranged from 11 to 13 percent of the pore volume. The nZVI suspension, containing either 10 g/L or 40 g/L CR-nZVI and 5.0 or 0.5 percent Tween 80, respectively, was then introduced into each column at a flow rate of 2 mL/min until CR-nZVI appeared in the column effluent. De-ionized water, containing 10 mM NaHCO_3 , was then introduced in a down-flow mode at a flow rate of 0.25 mL per minute for at least 75 pore volumes. Effluent samples were collected periodically and were analyzed for PCE, trichloroethene (TCE), cis-dichloroethene (cDCE), vinyl chloride (VC), and ethene content using a headspace gas chromatography (GC) method. At the conclusion of the water flushing, the contents of each column were extracted with iso-propanol and analyzed to determine the amount of entrapped PCE-DNAPL remaining in the column.

In first column experiment, conducted with 10 g/L CR-nZVI which yielded an Fe to PCE molar ratio of 0.53, approximately 9.5 percent of the residual PCE-DNAPL was displaced from the column during CR-nZVI introduction. Flushing with over the 239 pore volumes of water removed 49.6 percent of the PCE-DNAPL by dissolution based on column effluent data. Approximately 1.6 percent of the initial PCE-DNAPL was transformed to ethene, while 2.0 percent reacted to form TCE. At the conclusion of the experiment, the contents of the column were extracted, and indicated that 40 percent of the initial PCE mass remained in the column. These results are consistent with column experiments described in previous progress report,

where 2 percent of the PCE-DNAPL was displaced from the column during the introduction of a 10 g/L CR-nZVI suspension (Fe:PCE ratio of 0.72), 75 percent was removed by dissolution during 238 pore volumes of water flushing, 19 percent remained in the column at the conclusion of the water flushing period, and 4 percent was reacted to form daughter products that were detected in the column effluent.

In the second experiment, a 40 g/L CR-nZVI suspension containing 0.5 percent Tween 80 was introduced into a column containing residual PCE-DNAPL at a saturation of 11 percent, to yield an Fe to PCE molar ratio of 5.3. During the injection of 40 g/L CR-nZVI, less than 0.5 percent of the initial PCE-DNAPL was displaced from the column. After flushing with 78.4 pore volumes of water, approximately 44 percent of the PCE-DNAPL was removed by dissolution, while 18.5 percent was transformed to TCE and ethene. Thus, when the Fe to PCE molar ratio was increased by a factor of 10 (from approximately 0.5 to 5.0), the amount of PCE that reacted with Fe increased by a factor of 5. Here, it should be noted that the volume of water delivered in the second column experiments was approximately one-third of that used in first column experiment (10 g/L CR-nZVI).

The results of these column experiments demonstrate that (1) commercially-available nZVI can be effectively delivered into quartz sand containing residual DNAPL and (2) a portion of the PCE-DNAPL will react with the emplaced nZVI to form daughter products, including TCE and ethene. However, a substantial fraction of the residual PCE-DNAPL, up to 75%, simply dissolved in water and was recovered in the column effluent as the parent compound (i.e., dissolved phase PCE). These findings indicate that while we are able to deliver commercially-available nZVI products to source zones containing residual DNAPL with minimal mobilization of free product, the capacity of the co-located nZVI is unlikely to be adequate to effectively treat residual DNAPL-PCE. During the next project period, we will collaborate with Dr. Abriola's research group to develop and evaluate mathematical models that describe the delivery and reactivity of commercially-available nZVI in the column studies conducted to date. The coupling of experimental data and mathematical modeling will allow us to obtain time- and nZVI-dependent reaction rates in dynamic systems, which can then be used to assess the quantity and reactivity of nZVI that will be required to treat DNAPL source zones under various spill and hydrogeologic scenarios.

Presentations/Posters:

Kanel, S. R., Costanza J., Pennell K. D. Catalytic Reduction of Tetrachloroethene Dense Non-Aqueous Phase Liquid by Different Types of Reactive Iron Nano Particles, 237th ACS National Meeting and Exposition, in Salt Lake City, UT, USA, March 22-26, 2009.