

Injection of Nano Zero-Valent Iron for Subsurface Remediation: A Controlled Field-Scale Test of Transport

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ABSTRACT: A large, controlled nZVI injection experiment was conducted to compare transport distances predicted using a simple filtration model based on laboratory column experiments to observed field-scale transport. The column and model data indicated that a very high minimum velocity (~35 m/day) would be required to transport the nZVI through the subsurface. That velocity is difficult to maintain over distances of meters in medium sand or finer materials, but was accomplished using pairs of injection and extraction wells located 2.5m apart, which produced a hydraulic gradient of nearly unity. The data indicate that the nZVI was not transported as effectively as the laboratory data predicted. In addition, removal efficiencies within 5 cm of the injection well were significant and appeared to increase over time. The experiment highlights some of the challenges in transporting nZVI in the subsurface and points to the need for robust diagnostic tools for characterization of flow pathways and monitoring of nZVI transport.

BACKGROUND

Among emerging technologies for in situ remediation of subsurface contamination, injection of nano-sized zero-valent iron (nZVI) stands out for the sudden growth in interest it has attracted despite many uncertainties regarding its performance. We are aware of at least nine federal facilities that are early adopters of this technology, even though it is not clear—at this time—how this technology is best applied.

Much of the current optimism about this technology stems from the reported success of the first few field-scale demonstrations of nZVI injection for treatment of groundwater contaminated with chlorinated solvents. In each of these demonstrations, the distribution of emplaced nZVI and the ability of nZVI to degrade chlorinated solvent contaminants was assessed based on decreased chlorinated solvent concentration and changes in pH and/or oxidation/reduction potential (ORP) at a small number of down-gradient monitoring wells over a short period of time. Despite a number of well known uncertainties, these data have been interpreted as evidence that the injected nZVI was transported to where it reacted with the contaminants.

This interpretation of the field data is, however, at odds with the now extensive body of relatively-fundamental experimental and modeling work that has examined factors controlling nZVI mobility in porous media. The latter suggests that nZVI will, in general, have limited mobility in porous media unless several critical conditions are met. These include use of: (i) adequate amendment to the injected material to minimize agglomeration of the nZVI, (ii) very large velocities compared to typical regional groundwater flow velocities (i.e., pressurized injection conditions), and (iii) mechanical

enhancements to transport in granular media (i.e., induced fractures, pressure pulsing). Not all of these conditions were met in the field-scale demonstrations of nZVI injection that have been reported to date.

The contrast between the early pilot tests of nZVI injection and the more recent laboratory/modeling studies of nZVI behavior in porous media highlights the many uncertainties regarding the potential field performance of this technology. The three most important of these uncertainties are: (1) the types of data currently being used to characterize the mobility of nZVI at the field scale in granular media are inadequate; (2) it is unclear precisely what combinations of conditions are necessary for mobility of nZVI in the field. Recent work (esp. from SERDP ER-1485) has shown that successful emplacement requires minimizing agglomeration of the particles, and that agglomeration is affected by (i) the core material composition, which controls intra-particle magnetic forces, (ii) particle surface coatings, which influence electrosteric interactions with the particles, and (iii) injection velocity, which produces shear forces that inhibit agglomeration and particle attachment; and (3) there is very little known about what additional complications might arise at the field scale when nanoparticles are involved (e.g., flow bypassing due to the increased dimensionality of flow, variation of velocity gradients due to heterogeneity in the hydraulic conductivity field, and dilution and high velocity gradients with radial distance from the well.)

EXPERIMENTAL

To assess these issues we have conducted a well-controlled, field-scale demonstration of nZVI transport in a well-sorted medium sand aquifer. The aquifer is part of the Large Experimental Aquifer Program (LEAP) at OHSU. In this experiment, we were interested in transporting nZVI on a scale that was relevant to remediation systems (e.g., 2-3 meters). To accomplish this, and maximize the likelihood of transport, we installed an nZVI delivery system that included injection and extraction wells separated from one another by 2.5 m.

Preliminary laboratory data from column transport studies, collected using aquifer materials from the site and the nZVI chosen for this experiment, indicated that a velocity of 0.04 cm/s was necessary to achieve transport over a meter or more distance. To produce a linear velocity of 0.04 cm/s in the medium sand ($K = 0.02$ cm/s, porosity ~ 0.35) requires a hydraulic gradient close to unity. This is not difficult to produce in the immediate vicinity of the wells, but is difficult at distances of >0.5 m from the well.

A cross-section view of the experiment is shown in Figure 1. The dimensions of the aquifer are 10m x 10m x 3m deep. The injection and extraction wells had 0.75m screened intervals spanning the distance between two horizontal confining layers. To monitor hydraulic gradient between the wells, pressure monitoring points were installed 0.5 meters from the injection and extraction wells (i.e., 1.5m apart) and instrumented with submersible pressure transducers. Five discrete-level sampling points were located on the center line between the injection and extraction wells. An additional injection and extraction well pair (not shown) was installed either side of the well pair shown in Figure 1. The purpose of the additional wells was to constrain the lateral spreading of the injected nZVI and to help maintain a high velocity between the wells. The nZVI was injected at 2 gallons per minute (with comparable volumes of water injected in the adjacent wells) and a corresponding amount was withdrawn from the extraction wells.

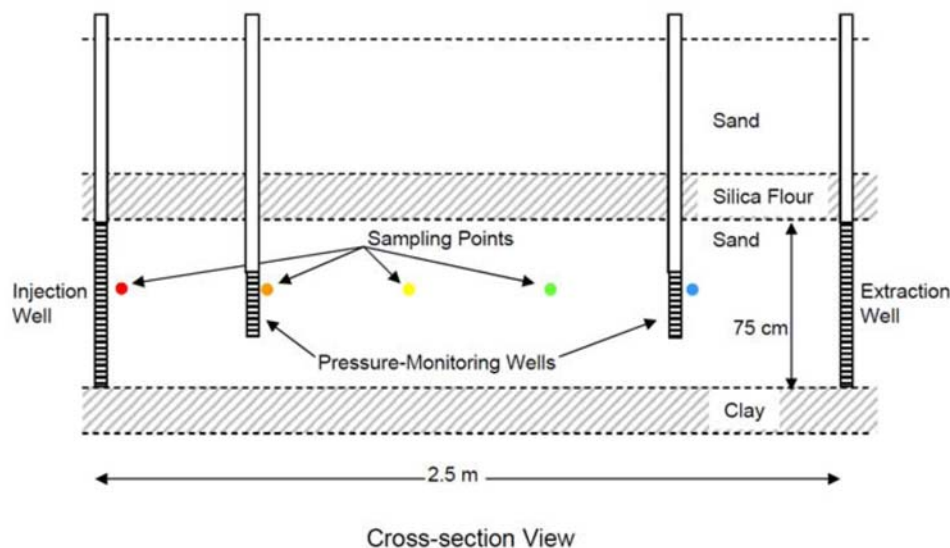


Figure 1. Cross section showing the injection and extraction wells, pressure monitoring wells and sampling points.

RESULTS AND DISCUSSION

The controlled nature of this experiments allowed detailed monitoring of a wide range of parameters in groundwater to track nZVI distribution, including 1) total iron; 2) dissolved oxygen (DO), 3) oxidation/reduction potential (ORP), 4) pH, 5) specific conductance, 6) light transmittance, 7) dynamic light scattering, and 8) chemical reduction of a probe contaminant (CCl_4)¹. To ensure that transport of the nZVI was accurately represented, the direct measurement of particulate iron concentrations was used as the indicator of nZVI transport. Based on those data (Figure 2), the maximum observed transport was about 0.5 m (i.e., less than the value predicted by the simple laboratory column studies.)

Contrary to the laboratory data and the use of a simple filtration model, which indicated high nZVI transmission efficiencies at high velocities, approximately 60% of the particles were filtered from the injected water within 5 cm of the well, and by the end of the experiment that value may have risen to as much as 90% of the injected mass. This removal indicates that there must have been significant deposition immediately around the well. Deposition could lead to at least two possible results that would explain the observed decrease in concentration over time at the 5 cm location. The first is that "filter ripening" could have increased the nZVI removal efficiency as a function of time. The second is that plugging due to that deposition could have caused changes in flow patterns around the injection well.

To examine these two possibilities we conducted a simple column experiment in which up to 100 pore volumes of nZVI (based on a 10-cm long column) could be injected to approximate near-well conditions during the injection. The linear velocity in the column was 0.167 cm/s, which is comparable to conditions near the well in the field-scale experiment. Both effluent iron concentration and injection pressure in the column were monitored.

¹ Manuscript for publication in Environmental Science & Technology is in preparation

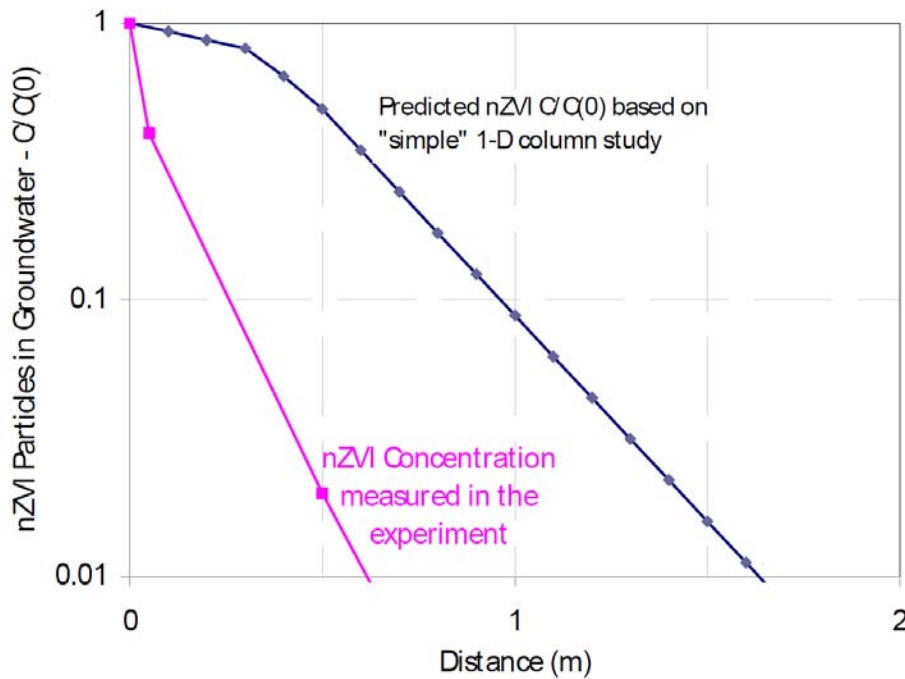


Figure 2. nZVI transport distance based on 1-D column studies and measured in the field-scale experiment.

The iron concentrations in the column effluent (normalized to the injection concentration) are shown in Figure 3. As expected, nZVI breakthrough occurred at about 1 pore volume. It rose to a $C/C(0)$ value of ~ 0.36 , which is consistent with both our earlier laboratory experiments and the observed field-scale experiment.

Figure 4 shows injection pressure for the column, which remained relatively constant during the first ~ 18 pore volumes, but then rose dramatically and exceeded the capacity of our pumping and monitoring systems before 25 pore volumes had been injected.

The iron effluent data for the column do not show a significant decrease in concentration with increasing number of pore volumes (although the column experiment could not be operated for as long a period as the field-scale experiment [>100 pore volumes] due to the dramatic pressure increase). As a result, our tentative conclusion is that the reduced concentration at the 5 cm location in the field-scale experiment may have been due to plugging near the injection well, and changes in flow pathways that resulted in less contact with the sampling point than had been the case at the outset of the experiment. This tentative conclusion is further supported by the observation of "daylighting" of the nZVI at several surface locations around the experiment. For this to have occurred, pathways must have been created through the low-permeability silica flour layer above the injection depth (possibly at locations where instrumentation was installed). We anticipate excavating the field-scale experiment in the coming months, and hopefully this will further identify the nZVI transport pathways.

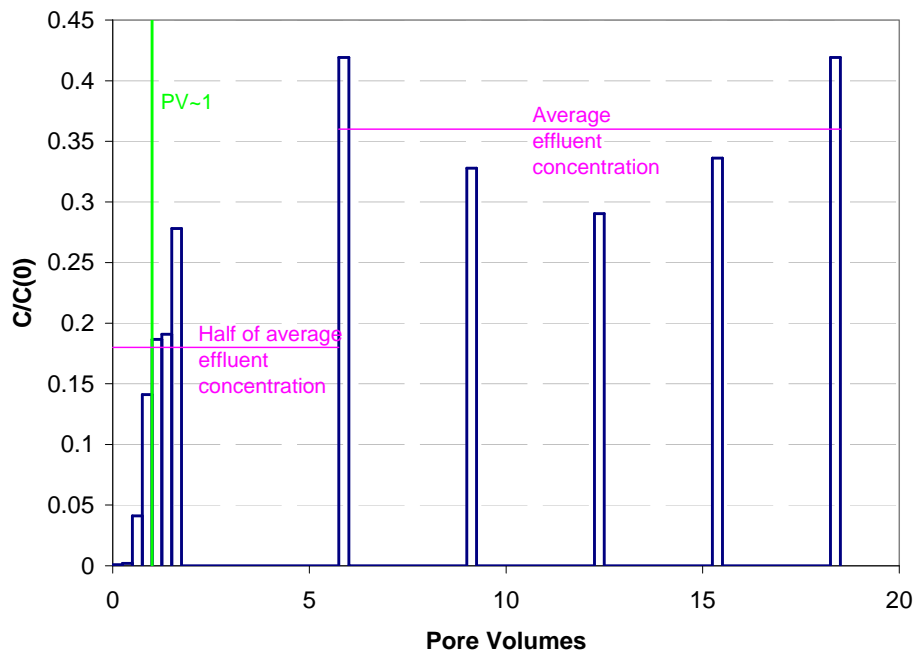


Figure 3. Normalized iron concentrations measured in column effluent samples (blue rectangles indicate the pore volume intervals for each water sample).

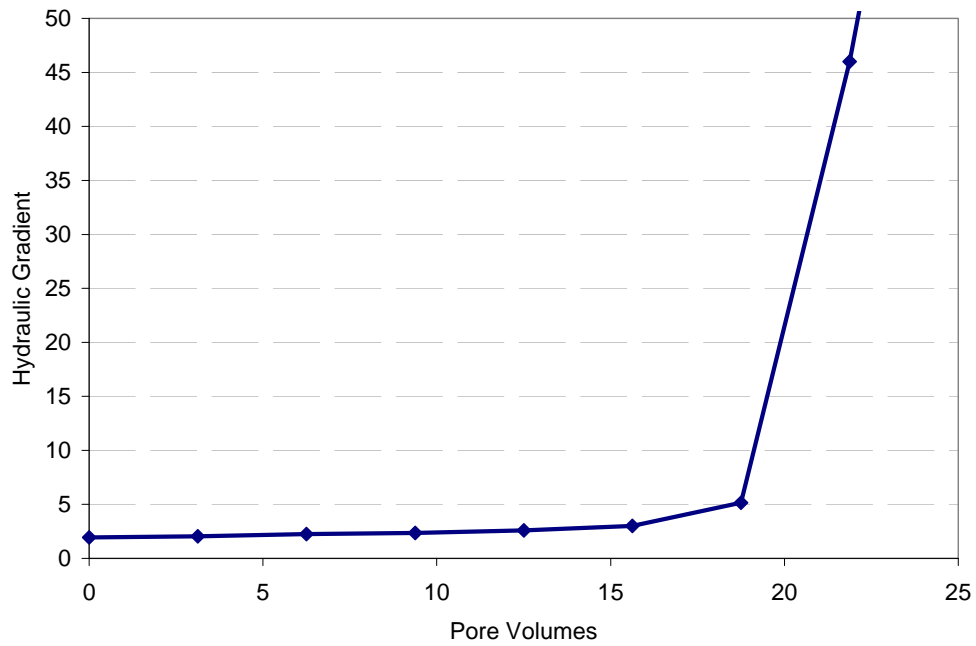


Figure 4. Measured hydraulic gradient across the 10cm long column as a function of pore volume.

CONCLUSIONS

Laboratory column data indicated that relatively high velocities were needed to achieve transport distances of greater than 1 meter. Field-scale experiment indicated that, if anything, the laboratory data were overly optimistic. A subsequent laboratory column experiment indicated that plugging of the aquifer materials near the injection well likely had a dramatic impact on the manner in which transport occurred, and likely resulted in decreased transport distances for the nZVI with time.

These data indicate that there is little reason to expect that field performance of nZVI transport will be any better than predicted by laboratory studies. However, the 3-D nature of most field settings makes prediction of actual performance difficult. As a consequence, robust protocols for designing nZVI injection strategies will require both a better fundamental understanding of nZVI transport processes, and better diagnostic tools for characterization of flow pathways and monitoring of nZVI transport).

ACKNOWLEDGEMENT

This work was supported by SERDP as part of ER-1485 (W912HQ-06-C-0038) and the U.S. EPA and National Science Foundation Center for Environmental Implications of Nanotechnology (CEINT) (EF-0830093).