Jet-Assisted Injection of Nano-scale, Zero-valent Iron to Treat TCE in a Deep Alluvial Aquifer

Paula R. Chang (paula.chang@erm.com ERM, Scottsdale, Arizona, USA)
Anthony D. Pantaleoni (Crane Co., Stamford, Connecticut, USA)
Douglas J. Shenk (ERM, Irvine, California, USA)

ABSTRACT: Nano-scale, zero-valent iron (nZVI) is extremely effective in rapidly treating high concentrations of chlorinated solvents such as trichloroethene (TCE). A common challenge in implementation of a chemistry-based technology in the saturated subsurface is optimizing the contact of the remediation amendment with the target chemical. In this case study, an innovative injection approach has been field-tested at a former aerospace manufacturing facility to overcome significant challenges posed by the low permeability of the soil and depth of the impacted groundwater. In order to maximize nZVI distribution and effectiveness, a 10,000-pound per square inch (psi) fracture lance injection tool was used to distribute the nZVI. Historic site soil and groundwater data was used to narrow the targeted injection interval to 108 to 118 feet (ft, 33 to 36m) below ground surface (bgs). Injection of 1,400 pounds of PolyMetallix™ was completed at two injection points spaced 15 ft apart over three days. Real-time oxidation-reduction potential (ORP) and pressure transducer data from downgradient groundwater monitoring wells showed separate radii of influence of at least 30 feet (9.1m). Groundwater data collected showed a TCE mass removal efficiency of 82 percent (%) to 96% within two weeks after completion of the injections.

INTRODUCTION

The site is a former Unidynamics facility, located in Goodyear, Arizona and is presently known as the Phoenix-Goodyear Airport-North Superfund Site. From 1963 - 1993, the site was used as a research, development, and manufacturing plant to produce ordnance components and electrochemical devices and systems used in defense and aerospace applications. Prior to 1974, small quantities (one to five gallons) of TCE were reportedly disposed of in two of four closely-spaced dry wells, which were located in the central portion of the site.

Several field tests were conducted near the dry wells using nZVI as a chemical reductant to remove TCE in groundwater. The field tests showed the permeability of the finer-grained layers of site soil (sandy silts and clays) to be inhibitory to gravity-fed nZVI injection. During the Phase I and Phase II pilot test efforts, the maximum injection mass of PolyMetallix™ nZVI was 50 lbs. PolyMetallix™ nZVI particles are manufactured by Polyflon, a Crane Co. Company, Norwalk, Connecticut under US Patent 7,641,971. The Phase I pilot test was conducted in January 2006 and the Phase II pilot test was conducted in June 2008. During the Phase II pilot test, 2,751 gallons (10,414 L) of nZVI solution was injected, at a concentration of 2.1 g/L, and under gravity-induced pressure head of 26 psi. The effects of the nZVI was measured in IRZ-IW-01, the well located 5 ft (1.5 m) downgradient of the injection point, indicating a radius of influence of at least 5 ft (1.5 m), and an estimated effective porosity of 0.31. The injection resulted in a two order of magnitude decrease in permeability at the injection location based on slug testing completed before and after injection (Arcadis 2008).

In order to overcome the variable lithology and maximize nZVI distribution and effectiveness for removing TCE and perchlorate from groundwater, a high pressure injection method for subsurface emplacement of nZVI was designed and implemented by ERM, Inc. (ERM) for Phase III of the field testing program. The Phase III pilot test was conducted in early February 2010.

REDUCTION CHEMISTRY

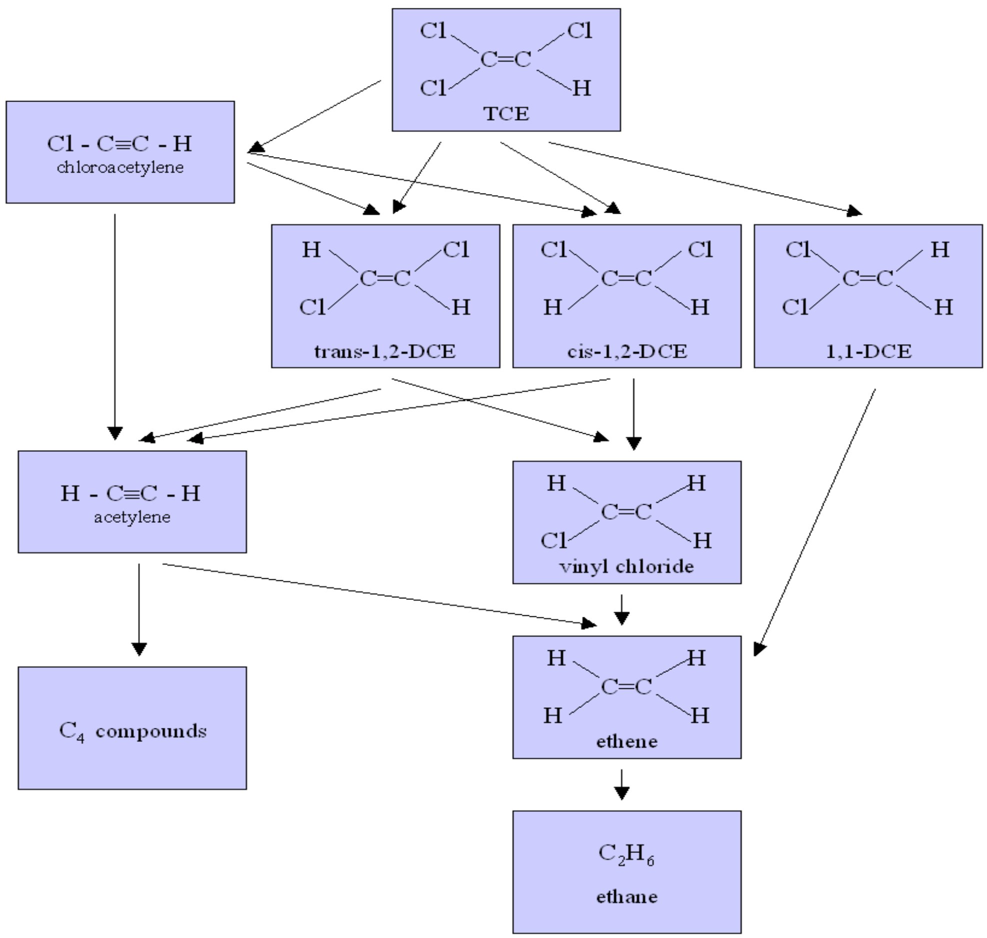

FIGURE 1. Hypothesized reaction pathways for the chlorinated ethene and other intermediates during reaction by ZVI.

The primary pathway for TCE reduction on zero-valent iron (ZVI) occurs primarily via a beta-elimination mechanism. This pathway involves a two-electron transfer in which chlorine atoms on adjacent carbons are released as chloride ions, with the concomitant formation of a triple bond (Arnold et. al. 2000; Farrel et. al. 2000). The resulting chloroacetylene then undergoes hydrogenolysis to form acetylene, which may then be further reduced to ethene or ethane (Figure 1).

The primary end products of TCE dechlorination by ZVI are ethane, ethene, and acetylene with the relative speciation dependant on the concentration of TCE, temperature, pH, and condition of the iron. By-products such as cis-1,2-dichloroethene, 1,1-dichloroethene and trans-1,2-dichloroethene can be produced by an alternate reaction pathway involving sequential dechlorination and account for less than 5% of the total degradation products.

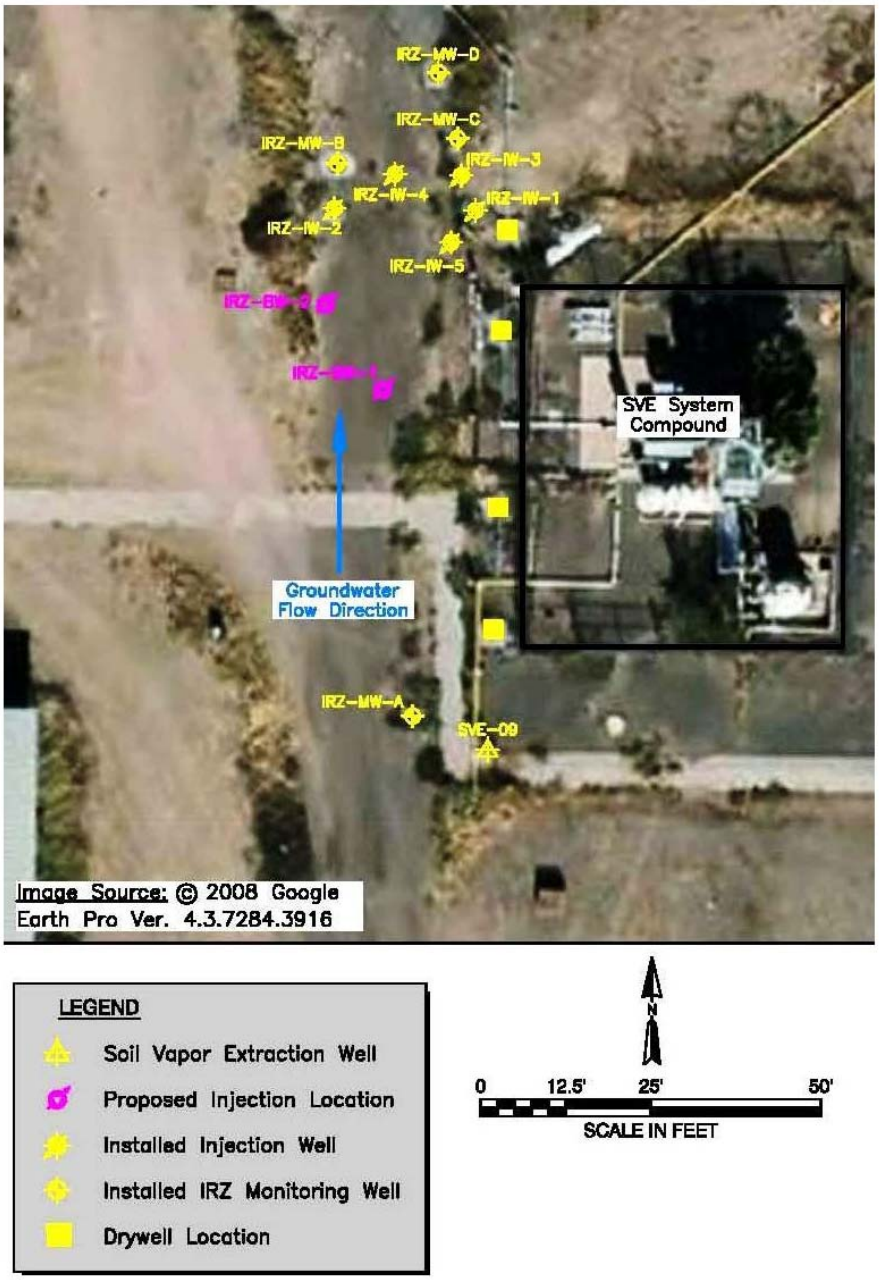

FIGURE 2. Pilot test injection and monitoring locations.

INJECTION DESIGN

A total of 7,421 gallons (28,091 L) of highly reducing (-500 to -800 mV) nZVI particles were injected into a deep alluvial water-bearing zone within the source area. PolyMetallix™ nZVI was provided by Polyflon as a 35.2 gram per liter aqueous solution contained in eighteen 275 gallon (1,041 L) totes.

Injections were conducted through two blank-cased injection wells at two intervals per well: 108 to 113 ft (33 to 34m) bgs and 113 to 118 ft (34 to 36m) bgs. Anaerobic water and an aqueous suspension of 21 g/L nZVI were alternately injected under pressure into each depth interval using a fracture lance multi-port injection tool positioned between two packers. A tri-plex pump capable of injection pressures of up to 10,000 psi was used to carve holes through the well casing, after which the nZVI solution was injected through a separate line by the lower pressure swing-arm pump. Alternating and sometimes simultaneous operation of the two pumps allowed for the jetted water to remove nZVI from the inside of the casing and promote mixing of the soil and the nZVI within the formation. The lower pressure pump was operated between 160 – 210 psi. Each tote of nZVI was batch-mixed with anaerobic water prior to injection using the lower pressure swing-arm pump. A total of 1,400 pounds of nZVI contained within a total volume of 7,421 gallons (28,091 L) of anaerobic water was injected into the 2 injection wells over three days.

MONITORING PROGRAM

Prior to start of injections, TempHion™ probes and pressure transducers were installed in six downgradient monitoring locations. The TempHions™ and pressure transducers were programmed to collect a measurement every 15 minutes. The TempHions are equipped to measure pH, temperature, and oxidation-reduction potential (ORP). The paired down-hole probes were placed at mid-screen, approximately 115 ft (35.05m) bgs at IRZ-MW-B, IRZ-MW-C, IRZ-MW-D, IRZ-IW-02, IRZ-IW-04, and IRZ-IW-05.

Pilot test groundwater monitoring included a baseline round, conducted prior to the injection of the nZVI particles, and groundwater sampling rounds performed at week 1, week 2, week 4, week 12, and week 24 after injection. The baseline sampling round was conducted on 10 through 12 January 2010, three weeks prior to the injection field work. Groundwater samples were analyzed for VOCs, perchlorate, chlorate, chlorite, and hydrogen during every sampling event. During select monitoring rounds periodic samples were taken to monitoring changes in total and dissolved iron, manganese, chloride, sulfate, nitrate, alkalinity, sodium, phosphate, total organic carbon in groundwater during the monitoring period.

RESULTS

Injection Radius of Influence. The ORP, pH, temperature, and water level data taken during the injections showed direct responses to the injections conducted at IRZ-BW-1 and IRZ-BW-2. A decrease in ORP to less than -800 milliVolts (mV) at IRZ-IW-2, located approximately 12 ft (3.7m) from the injection point, was observed within a few minutes of the start of injection at IRZ-BW-2. Measurements taken by a hand-held field instrument at IRZ-MW-B also showed a drop in conductivity within a similar timeframe.

IRZ-IW-4 showed a strong response to the injections conducted at IRZ-BW-1 with a similar decrease in ORP, and increases in pH, temperature, and water level elevation, also occurring within minutes of the start of injection. IRZ-IW-4 is located 30 ft and 3 inches (9.2m) from IRZ-BW-1. Significantly elevated concentrations of hydrogen were detected in the week 1 and week 2 post-injection sampling events at all groundwater monitoring locations. Hydrogen concentrations began to decline after week 1 in monitoring wells located within the injection radius of influence, but groundwater from wells outside the injection area showed increasing trends in hydrogen after the second week groundwater monitoring event, indicating the downgradient migration of nZVI treated groundwater.

Treatment Effectiveness. TCE concentrations in groundwater samples from IRZ-MW-B, IRZ-IW-2, and IRZ-IW-4 decreased between 82% and 96% between the baseline and week 2 sampling events. TCE concentrations at IRZ-MW-B decreased from 46 µg/L to 1.7 µg/L. TCE concentrations at IRZ-IW-2 and IRZ-IW-4 decreased from 510 µg/L to 93 µg/L, and 2,300 µg/L to 280 µg/L, respectively. Between week 2 and week 4, TCE concentrations began to recover, with the exception of IRZ-MW-B, where the TCE concentration has remained at 1.7 µg/L.

TCE concentrations temporarily increased at groundwater monitoring locations outside of the radius of influence of the nZVI indicating that the injections did result in the movement of groundwater containing higher concentrations of TCE into those areas. Former injection well IRZ-IW-5 was the injection well for the Phase II pilot test, and due to the loss of permeability in the vicinity of this well, it is suspected that the Phase III injectate may have bypassed this location, and that the low permeability of the soil may have prevented access to the area near IRZ-IW-01. The continued low permeability conditions in the vicinity of IRZ-IW-05 is evidenced by the ORP, which has remained at -500 mV since the Phase II pilot injection performed in April of 2008.

CONCLUSIONS

Jet-assisted injection was effective in delivering a significant mass of nZVI to a distance of at least 30 feet from the injection points. Treatment efficiencies for TCE of up to 96% were observed during early post-injection monitoring. The data and field observations collected during this pilot test by ERM will be used as the basis for a full-scale application of in-situ chemical reduction using PolyMetallix™ nZVI to treat TCE in the source area of this site. ERM anticipates that application of this technology within the source area will significantly reduce the cost, magnitude, and longevity of ongoing groundwater extraction and aboveground treatment activities.

REFERENCES

Arcadis, 2006, Final – Draft Main Drywells Source Area Characterization Report, Phoenix-Goodyear Airport – North Superfund Site, Goodyear, Arizona, November 20.

Arcadis, 2008, Technical Memorandum #5 - Summary of Field Implementation and Results for the Phase II Nano-Scale Zero Valent Iron Field Testing Program, Phoenix-Goodyear Airport-North Superfund Site, Goodyear, Arizona, December 23.

Arnold, William and A. Lynn Roberts. 2000. *Pathways and Kinetics of Chlorinated Ethylene and Chlorinated Acetylene Reaction with Fe(0) Particles*. ES&T. Volume 34, Number 9.

ERM, 2009, NZVI Pilot Test Work Plan for Phase III of the Field Testing Program, Phoenix-Goodyear Airport-North Superfund Site, Goodyear, Arizona, November.

Farrel, James, Mark Kason, Nicos Melitasm and Tie Li. 2000. *Investigation of the Long-Term Performance of Zero-Valent Iron for Reductive Dechlorination of Trichloroethene*. Environmental Science and Technology. Volume 34. Number 3.