Environmental Solutions

In Situ Chemical Reduction vs. Enhanced Reductive Dechlorination Case Study

PROJECT

Comparison of *In Situ* Chemical Reduction (ISCR) to enhanced reductive dechlorination to treat trichloroethene in an aerobic aquifer.

Site: Concord Naval Weapons Base in Concord, CA

SUMMARY

In Situ Chemical Reduction (ISCR) was compared to enhanced reductive dechlorination (ERD) to treat groundwater affected by trichloroethene (TCE). Two pilot tests were conducted that compared the rates of contaminant degradation as well as other biogeochemical processes of both processes. The ISCR process was demonstrated to degrade the TCE substantially faster than the ERD process while minimizing the generation of vinyl chloride. ISCR is currently being applied to treat the extended TCE plume.

CHALLENGE

The Concord Naval Weapons Station (CNWS) facility is located in Concord CA and is included in the Base Realignment and Closure (BRAC) program. Soil and groundwater at Installation Restoration (IR) Site 29 at the CNWS facility has been affected by a discharge TCE. The affected aquifer consists of unconsolidated silt, sands and clays. Groundwater, which is encountered approximately 50 feet below ground surface, is highly aerobic (dissolved oxygen (DO) ~7 mg/L) and mildly oxidizing (oxidation reduction potential (ORP) ~250 millivolts (mV). The source of TCE is a building previously used to refurbish munitions. TCE was discharged, likely through drain lines, in a source are east of the building. The TCE plume extends approximately 700 feet down hydraulic gradient from the source area and up to 100 feet below ground surface. The site is shown on Figure 1.

Figure 1: TCE plume at IR Site 29 at Concord Naval Weapons Station

Enhanced Reductive Dechlorination Pilot Test:

An Enhanced Reductive Dechlorination (ERD) pilot test was previously conducted in the TCE source area from 2011 to 2014. The ERD pilot test used buffered emulsified vegetable oil substrate which was augmented with dechlorinating microbial consortium (SDC-9™). Sodium lactate was added to the injection water to condition the water prior to bioaugmentation. Injections were conducted from 50 to 65 feet below ground surface (bgs) at 2.5 foot vertical intervals in locations 12 foot on center to achieve a 6.5 foot radius of influence. The degradation of CEs during the ERD pilot test was measured in wells S29MW10 and S29MW11. The ERD pilot test demonstrated that application of resulted in complete degradation the TCE and daughter products concentration from

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approximately 5,000 microgram per liter (μg/L) to less than 1 μg/L in approximately 550 days. However, arsenic concentrations were observed to increase during the test. The ERD pilot test area is shown on Figure 2.

The Navy intends divest the property under the Base Realignment and Closure (BRAC) program as rapidly as possible. To achieve this goal, the Navy requested an approach that would aggressively treat the TCE, reduce the potential for daughter products and maintain conditions conducive to continued reductive dechlorination for a longer duration.

SOLUTION

In Situ Chemical Reduction (ISCR) was selected for evaluation enhance the ERD process demonstrated to be applicable during the initial ERD pilot test. The ISCR process was selected because it combines benefits of biotic processes previously demonstrated to be applicable at the site, and abiotic processes which enhance the biological process. ELS™ Microemulsion, a lecithin-based substrate of food grade carbon, was selected for the biotic degradation of TCE. ELS was selected for the organic substrate because of its longevity as a substrate, high electron donor capacity, enhanced transport characteristics, and because essential nutrients nitrogen and phosphate are included in the molecular structure of the molecule. Zero valent iron was also incorporated to enhance abiotic degradation to reduce the potential for generation of toxic degradation products. The abiotic degradation process primarily bypasses the generation of these toxic degradation product by the β-elimination pathway which temporarily generates unstable chlorinated acetylenes which may be converted to ethene and ethane.

ISCR Pilot Study: A Design Optimization Test (DOT) was conducted to compare the ISCR approach to the previously evaluated ERD approach. The DOT was conducted in the TCE source area in wells (S29MW01 and S29MW03) not affected by the ERD pilot test. The ERD and ISCR test wells and injection locations are shown on Figure 2. The DOT was conducted by distribution of the ISCR substrate at 3 locations located at a distance of 10 feet from wells S29MW01 and 3 locations at a distance of 15 feet from S29MW03. At each vertical interval, the aquifer was first primed for substrate distribution by fracturing the aquifer using the ELS and bioaugmentation solution.

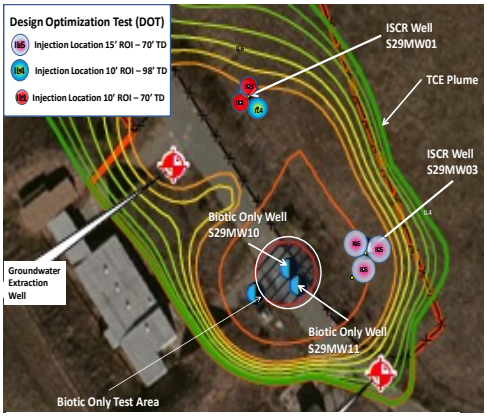

Figure 2: ISCR and ERD pilot test wells and injection locations

Following confirmation of fracture development, ZVI suspended in guar was injected into the interval followed immediately by the lactate, ELS solution and bioaugmentation culture. Monitoring was then conducted to verify the degradation of TCE.

Pilot Test Analytical Results: The following graphs compare the results of the ERD and ISCR pilot tests.

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pH: The hydrogen ion activity (pH) substantially affect the biological reductive dechlorination has been demonstrated to be inhibited by low pH conditions Dehalococcoides (Dhc). Below pH of 6.0 Standard Units (SU), the degradation rate of CEs begins to decrease and at pH 5.0 SU Dhc stop degradation. Therefore maintaining pH in a range favorable to reductive dechlorination is critical for effective application of ERD.

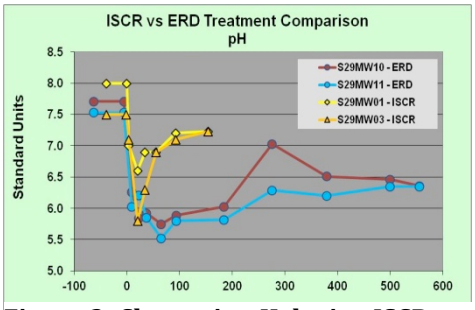

Figure 3: Change in pH during ISCR and ERD pilot tests

Following injection, the pH of the groundwater in the ERD test gradually decreased to 5.52 SU (Day 66) and required 200 days to return to favorable conditions (>6.0 SU). Whereas pH only fell below 6.5 in one well (pH 5.8 SU, well S29MW03) and had returned to favorable conditions the following sample event (Day 35) and maintained pH within the favorable range for the duration of the DOT.

Although excursions of pH outside the range favorable to biological degradation do not affect the abiotic degradation of the CEs by the zero valent iron (ZVI), the ZVI injected with the ELS act to maintain the pH within a range favorable to biological reductive dechlorination. The pH of the pilot tests is presented in Figure 3.

Arsenic: During the establishment of highly reducing condition necessary for reductive dechlorination, dissolved arsenic (As) concentration increases as insoluble As(V) is reduced to soluble As (III). The increase in As during establishment of reducing conditions can result in concentrations of this contaminant to regulatory levels. During the ERD pilot test, dissolved As concentrations increased to over 0.050 mg/L and maintained concentrations in excess of the primary drinking water standard (0.010 mg/L) for the duration of the pilot test. During the DOT however, only slight increases in As were observed and those concentrations never exceeded the primary drinking water standard. The change in As concentrations in the two tests are shown in Figure 4.

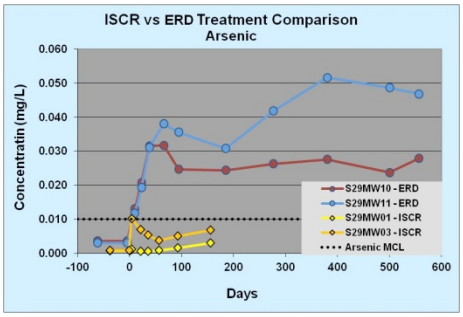

Figure 4: Change in arsenic concentration in ISCR and ERD pilot tests

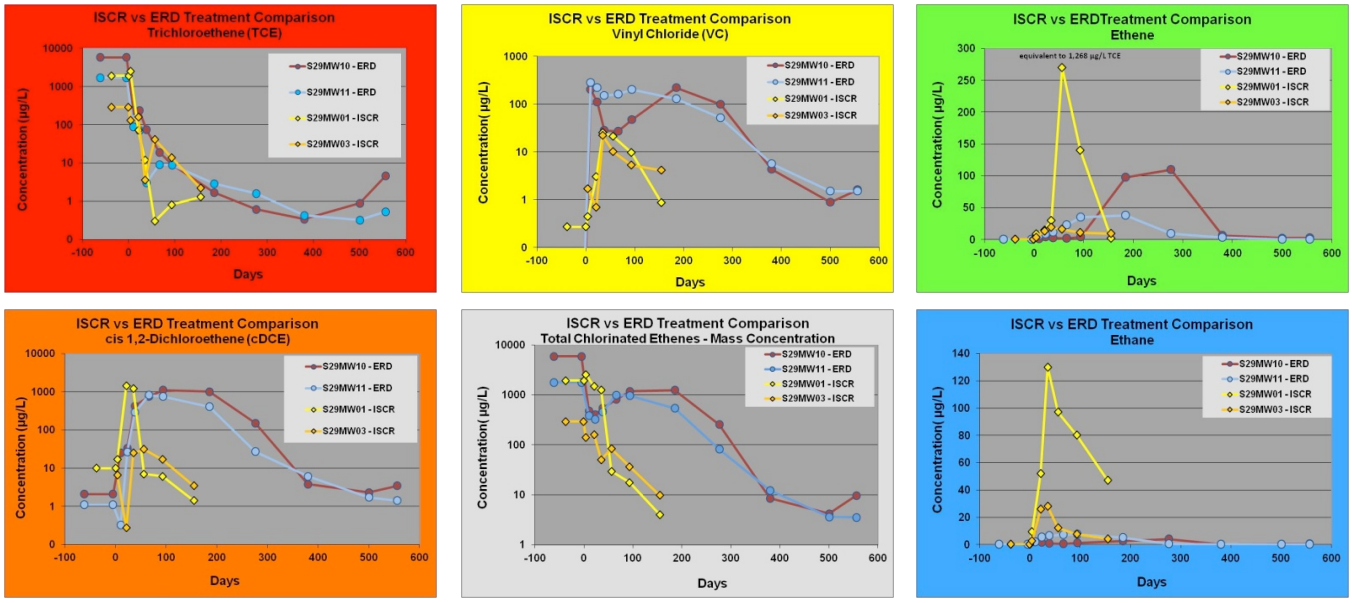

Figure 5: Change in ethenes, and ethane concentration during ISCR and ERD pilot tests

VOCs: As highly reducing conditions were established, rapid reductive dechlorination of the TCE was observed in both the ERD and ISCR tests. Notable differences were observed in the production and degradation of chlorinated daughter products dichloroethene (DCE) and vinyl chloride (VC) in the two tests. Cis 1,2-DCE concentrations increased substantially in both tests, however, DCE degradation occurred much more rapidly in the ISCR test. As DCE concentration decreased concentrations of VC increased in both tests, however at substantially lower concentrations in the ISCR test. The minor production of VC indicates that the β-elimination pathway is the primary DCE degradation pathway. The persistence of DCE, and resulting generation and degradation of VC, and the higher ratio of VC generated by DCE reduction by ERD processes appears to be the primary reason for the longer remedial time when applying ERD approach to this site.

Complete reductive dechlorination of the CEs was confirmed by the near stoichiometric conversion of the CEs to ethene and ethane (270 and 130 micrograms per liter; µg/L respectively well S29MW01) observed by Day 56 of the DOT. The results of the total CE concentration decreased at a much faster rate by ISCR in the DOT than in the ERD Test. This resulted in a reduction of total mass concentration of 99.8 % within 155 days. Whereas, 500 days was required in the ERD test to achieve the same amount of mass reduction.

The molar fraction of the chlorinated ethenes, and ethene, ethane and acetylene was plotted on pie charts to evaluate the extent of dechlorination. The sequential reduction of chlorinated ethenes TCE (red) to DCE (orange) VC (yellow) to non toxic degradation products ethene (green), ethane (blue), and acetylene (purple) are presented in Figure 6. The pie charts demonstrate that the process ISCR process (shown in the bottom two rows) more rapidly advanced the sequential dechlorination than the ERD process (shown in top two rows). The presence of ethane in the ISCR process also demonstrates that the reductive process continued after the generation of ethene indicating that more strongly reducing conditions and hydrogen

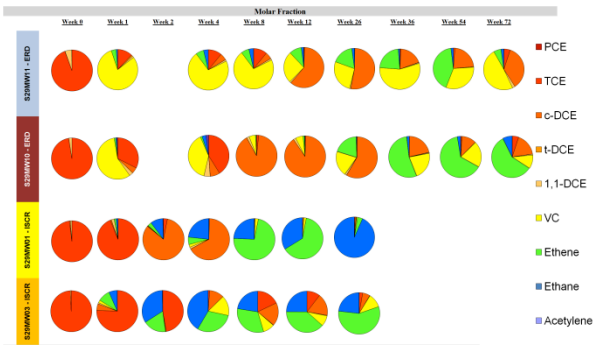

Figure 6: Change in total molar concentration during ISCR and ERD pilot tests

RESULTS

The data collected during the DOT and Biotic Only pilot allowed for a comparison of ISCR to standard enhanced reductive dechlorination. The data demonstrate that the ISCR process had substantial advantages over the Biotic Only approach to remediation. These benefits advantages include the following:

- The ISCR process can be effectively applied in highly aerobic aquifers.
- The ZVI in the ISCR approach buffered the aquifer and maintained the pH within the favorable range for biological reductive dechlorination, whereas pH remained below the optimal level for a substantially longer period of time thereby reducing the degradation rate.
- The ISCR process maintained the dissolved arsenic concentration below the MCL whereas arsenic has exceeded the MCL by a factor of 3 to 5 for more than 500 days and does not appear to be decreasing
- Degradation of each of the chlorinated ethenes was substantially faster in the ISCR pilot test than in the ERD pilot test. The longer time for dechlorination in the ERD pilot test is considered to be attributable to the slow biotic reductive dechlorination of cis 1,2-DCE and VC compared to the more rapid abiotic degradation of cis 1,2-DCE and the ERD of residual VC generated during the ISCR process.
- The pie charts indicate that the CEs are more rapidly converted to primarily non toxic degradation products by the ISCR process than by the ERD process.

CONCLUSION

In Situ Chemical Reduction, represents a significant improvement to standard enhanced biological reductive dechlorination for treatment of CEs. The symbiotic processes which constitute the ISCR approach more rapidly achieve the remedial goals than ERD processes alone. ELS was confirmed to be highly effective electron donor for biologically enhanced reductive dechlorination processes in the ISCR technology. Significantly, the primary degradation process of the cis 1,2-DCE was abiotic β-elimination resulting from contact with the incorporated ZVI.

This process was demonstrated to be much quicker than the degradation of cis 1,2-DCE by ERD and minimized the production of VC.

The ELS was demonstrated to rapidly established highly reducing conditions which were buffered by the incorporated ZVI. The combination of these biotic and abiotic processes established conditions whereby the supplied bioaugmentation culture efficiently dechlorinated the minor amount of residual VC. The remedial goals for this project were achieved within the DOT area within 155 days as compared to more than 500 days using the ERD approach. The application of this technology provides the contractor with a mechanism for rapidly achieving site remedial goals which is essential in performance based contracts. Ultimately, the reduced remedial time allows for the Navy to achieve its goal of divesting the base in a timely fashion.

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