Field and Laboratory Evaluation of the Treatment of DNAPL Source Zones Using Emulsified Zero-Valent Iron

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Emulsified zero-valent iron (EZVI) is a surfactant-stabilized, biodegradable emulsion that forms droplets consisting of a liquid-oil membrane surrounding zero-valent iron (ZVI) particles in water. This article summarizes the results obtained during the first field-scale deployment of EZVI at NASA's Launch Complex 34 (LC34) located on Cape Canaveral Air Force Station, Florida, in August 2002 and presents the results of recent follow-on laboratory tests evaluating the mechanisms, which contribute to the performance of the technology. The field-scale demonstration evaluated the performance of EZVI containing nanoscale zero-valent iron (NZVI) when applied to dense, nonaqueous phase liquid (DNAPL) trichloroethylene (TCE) in the saturated zone. Results of the field demonstration indicate substantial reductions in TCE soil concentrations (greater than 80 percent) at all but two soil boring locations and significant reductions in TCE groundwater concentrations (e.g., 60 percent to 100 percent) at all depths targeted with EZVI. Laboratory tests conducted in 2005 suggest that both NZVI particles and EZVI containing NZVI can provide significant reductions in TCE mass when used to treat TCE DNAPL in small test reactors. However, EZVI was able to reduce TCE concentrations to lower levels than were obtained with NZVI alone, likely as a result of the combined impact of sequestration of the TCE into the oil phase and degradation of the TCE with the NZVI. © 2006 Wiley Periodicals, Inc.

INTRODUCTION

Significant laboratory and field research has demonstrated that zero-valent metals will reductively dechlorinate dissolved chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE) to ethene in groundwater (Gillham & O'Hannesin, 1994; Powell et al., 1998). Permeable reactive barriers (PRBs) containing zero-valent iron (ZVI) as the reactive material have been shown to be effective in treating plumes of dissolved chlorinated solvents (O'Hannesin & Gillham, 1998; Vogan et al., 1999). PRB technology is passive and requires no energy; however, it still relies on dense nonaqueous phase liquid (DNAPL) dissolution and transport of dissolved chlorinated solvents to the PRB for treatment, and, therefore, PRBs do little to reduce the cleanup time for sites where DNAPL is present. Nanoscale ZVI (NZVI) particles, either in a water slurry or as particles contained within an oil emulsion droplet (EZVI), have advantages over the conventional PRB applications since they may be injected deeper in the subsurface than is practical for conventional PRBs, and can be injected directly into DNAPL source areas to treat these areas directly. Nanoscale ZVI particles also have a much greater surface area than microscale or granular ZVI and, therefore, degrade contaminants at a faster rate.

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Nanoscale Zero-Valent Iron Technology Description

Laboratory and field tests have demonstrated that treatment of chlorinated ethenes, such as TCE, with NZVI particles is more rapid than with conventional forms of granular iron (Elliott & Zhang, 2001; Lien & Zhang, 1999; Lowry & Johnson, 2004; Wang & Zhang, 1997). Nanoscale ZVI is also more reactive than microscale ZVI or iron powders because the smaller particle size gives the NZVI a larger surface area per unit mass. The degradation of chlorinated solvents by ZVI regardless of particle size is believed to occur via both β-elimination and reductive dechlorination at the iron surface and require excess electrons produced from the corrosion of the ZVI in water (Arnold & Roberts, 2000). The β-elimination pathway involves the conversion of TCE, for example, to chloroacetylene, which is further dechlorinated to acetylene. Acetylene is subsequently degraded to ethene and ethane. Some degradation may also occur via sequential dechlorination where the target chemicals undergo sequential dechlorination steps, resulting in the formation of nonchlorinated hydrocarbon products (e.g., ethene and ethane).

Due to their very small size, NZVI particles may remain in suspension in groundwater and migrate downgradient of an injection point with the flow of groundwater.

As a result of their high reactivity, NZVI particles are quickly surrounded by a passivating layer—such as a shell of oxide, which limits the ZVI corrosion rate (Nurmi et al., 2005). Zhang (2003) demonstrated that NZVI particles could remain reactive for six to eight weeks in a water suspension in the laboratory. However, these highly reactive nanoscale particles change over time, with handling, during storage (in a slurry of water), and with exposure to natural environments where constituents in groundwater will decrease the reactivity of the particle surface.

Due to their very small size, NZVI particles may remain in suspension in groundwater and migrate downgradient of an injection point with the flow of groundwater (Elliott & Zhang, 2001). Some researchers (Schrick et al., 2004), however, have questioned the mobility of NZVI in typical groundwater situations. The NZVI particles will agglomerate in many groundwater situations to form larger particles that are in the micron-size range. Although it is possible to form stable suspensions of nanoscale particles (Schrick et al., 2004), aggregation of nanoscale particles may be difficult to avoid under most environmental conditions (Nurmi et al., 2005). This aggregation of the particles may result in particle filtration by aquifer material preventing them from migrating with the flow of groundwater.

Although NZVI particles can be injected into deep contaminant zones and source areas, the ZVI particles require water for the degradation reactions to occur. Therefore, injecting the particles into a DNAPL source zone will still require the dissolution of the DNAPL into the surrounding water before degradation can occur. The rapid degradation of dissolved-phase TCE by the fast-reacting NZVI may, however, enhance the dissolution of the DNAPL and reduce the cleanup time for source zone DNAPL (Seagren et al., 1993).

Emulsified Zero-Valent Iron Technology Description

EZVI can be used to enhance the destruction of chlorinated DNAPL in source zones by creating intimate contact between the DNAPL and the ZVI particles. The EZVI is composed of food-grade surfactant, biodegradable oil, water, and ZVI particles (either nano- or microscale iron), which form emulsion particles (or droplets) that contain the ZVI particles in water surrounded by an oil-liquid membrane (Quinn et al.,

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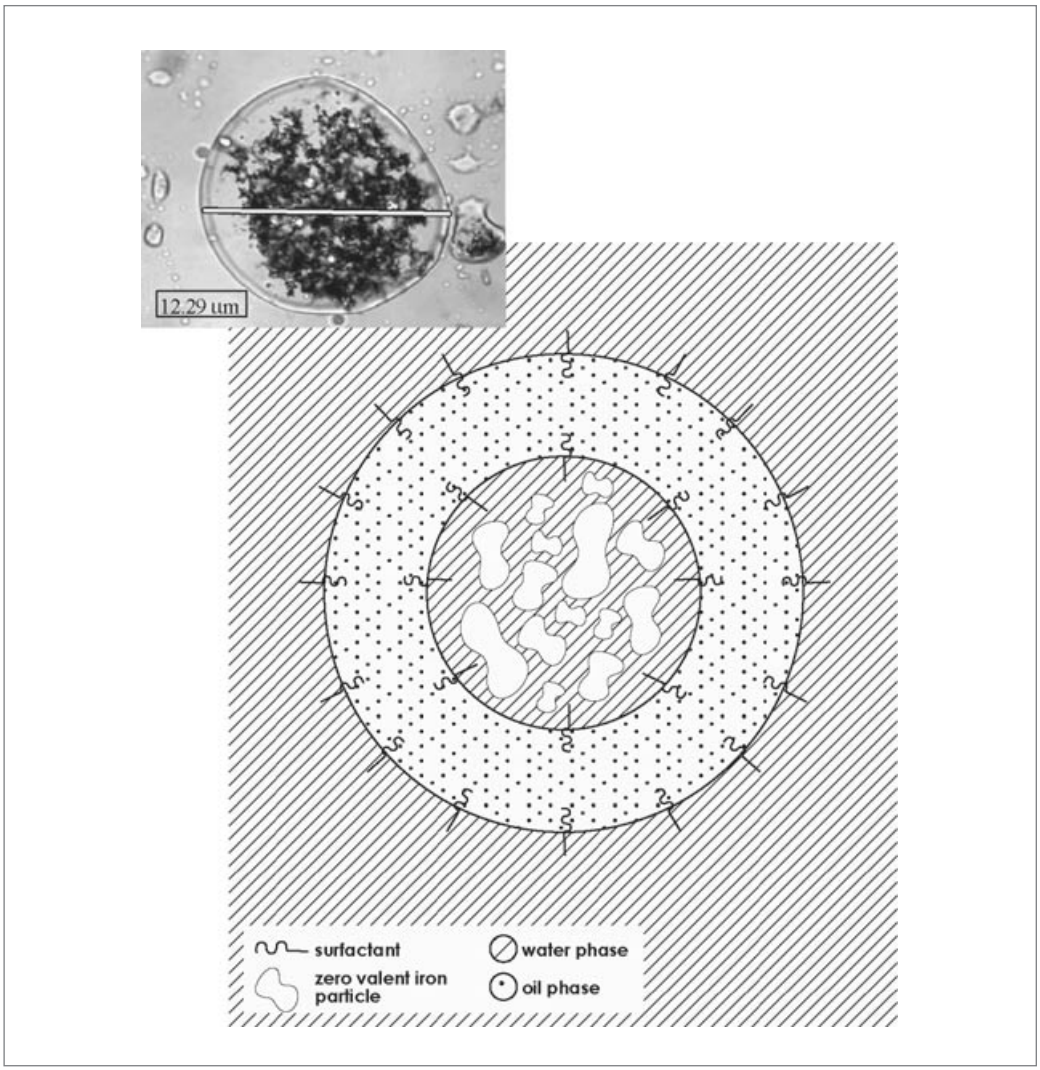

Exhibit 1. Magnified image and schematic of emulsion droplet

2005). Exhibit 1 shows a schematic and a magnified image of an emulsion droplet. Since the exterior oil membrane of the emulsion particles has hydrophobic properties similar to that of DNAPL, the emulsion is miscible with the DNAPL (i.e., the phases can mix). It is believed that as the oil emulsion droplets combine, for example, with pure-phase TCE, the TCE dissolves and diffuses into the aqueous droplet containing ZVI that resides within the oil emulsion droplet. It is also believed that the final degradation by-products from the dechlorination reaction are driven by the increase in concentration inside the aqueous emulsion droplet to diffusion out into the nonaqueous phase (oil and TCE), then out into the surrounding aqueous phase (Brooks, 2000). While the ZVI particles in the aqueous emulsion droplet remain reactive, the chlorinated compounds are continually degraded within the aqueous emulsion droplets, thus maintaining a concentration gradient across the oil membrane and establishing a driving force for additional TCE migration into the aqueous emulsion droplet, where additional degradation can occur.

The primary application of the EZVI technology is treatment of DNAPL source zones, but it is also capable of treating dissolved-phase chemicals. EZVI that is located near DNAPL will also degrade the dissolved-phase chemicals that it contacts. The reduction in concentration of dissolved-phase chemicals in the vicinity of the DNAPL will enhance mass dissolution from the DNAPL. EZVI that is located away from the source will also reduce concentrations of contaminants in the dissolved plume.

In addition to the abiotic degradation associated with the ZVI, the injection of EZVI containing vegetable oil and surfactant will result in sequestration of the chlorinated ethenes into the oil and biodegradation of dissolved chlorinated ethenes. Chlorinated solvents will preferentially dissolve into the oil component of the EZVI, thereby reducing the aqueous phase concentrations. The chlorinated solvents may then be degraded by the ZVI in the EZVI. The vegetable oil and surfactant can also act as electron donors to promote anaerobic biodegradation of the chlorinated solvents. Abiotic degradation resulting from the ZVI in the EZVI was shown to be a very fast process in laboratory studies conducted at the University of Central Florida (Quinn et al., 2005). If the amount of ZVI is not sufficient to completely degrade all of the TCE in the source area to ethane, then the vegetable oil and surfactant can act as a slow-release electron donor for biodegradation processes (Major et al., 2002).

. . . the hydrophobic membrane surrounding the NZVI protects it from other groundwater constituents, such as some inorganic compounds, that might otherwise react with the NZVI, reducing its capacity or passivating the iron.

Another potential benefit of EZVI over NZVI for environmental applications is that the hydrophobic membrane surrounding the NZVI protects it from other groundwater constituents, such as some inorganic compounds, that might otherwise react with the NZVI, reducing its capacity or passivating the iron. While the oil membrane of the EZVI will allow organic constituents (TCE and other ethenes) to diffuse through the liquid membrane and contact the NZVI, it will inhibit diffusion of other ionic constituents and limit their contact with the NZVI. This mechanism potentially reduces the mass of NZVI required for treatment relative to unprotected NZVI.

SUMMARY OF FIELD-SCALE DEPLOYMENT AT LAUNCH COMPLEX 34

In August 2002, the first field-scale deployment of EZVI took place at NASA's Launch Complex 34 (LC34) on Cape Canaveral Air Force Station, Florida. The small demonstration was conducted by GeoSyntec under a grant from NASA and independently evaluated under the US EPA's Superfund Innovative Technology Evaluation Program. Based on predemonstration groundwater and soil sampling, a test plot was selected that was 15 feet long $\times$ 9.5 feet wide $\times$ 26 feet deep. This plot consists of an upper portion of the site's surficial aquifer known as the Upper Sand Unit (USU) (see Exhibit 2). The Upper Sand Unit (USU) is underlain by a Middle Fine-Grained Unit, which constitutes a semiconfining barrier to the Lower Sand Unit below. The EZVI treatment was targeted at depths of 16 to 24 feet below ground surface (bgs) where most of the DNAPL within the USU was found to reside. The pilot test layout is fully described in Quinn et al. (2005) but contained injection and extraction wells that were used to maintain hydraulic control over the test area, a row of upgradient and downgradient monitoring wells, and eight EZVI injection points.

During the field demonstration, a total of 661 gallons of EZVI, containing 770 lbs of NZVI was injected into the USU along with 1,627 gallons of site groundwater. Pressure pulse technology was used to inject the EZVI over a four-day period. Exhibit 3 shows the site plot and actual injection taking place underneath the facility's floor slab.

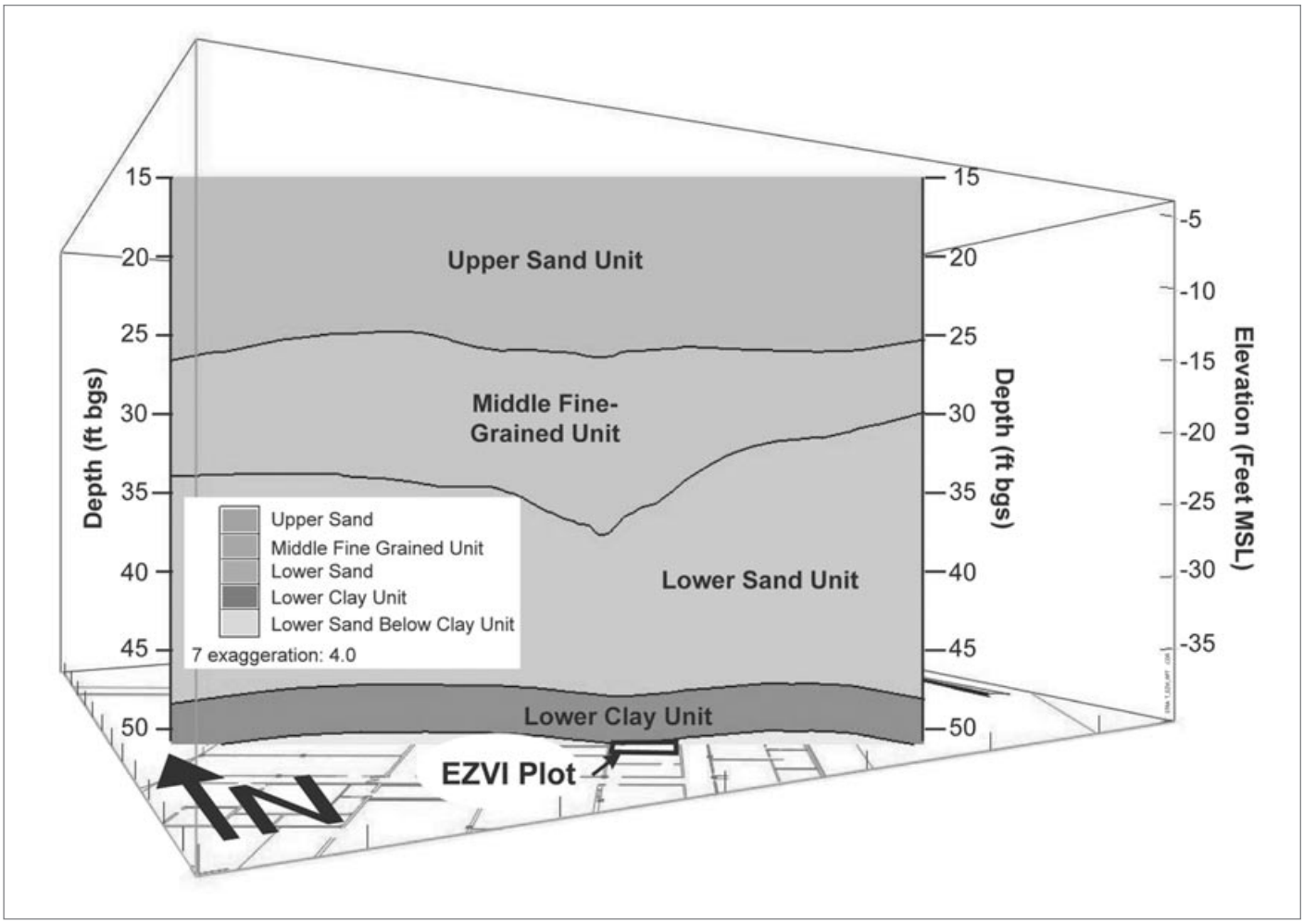

Exhibit 2. Launch Complex 34 site lithology

Exhibit 3. EZVI injection using pressure pulse technology

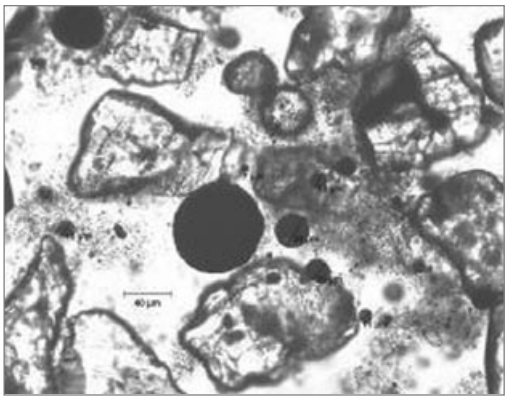

Exhibit 4. Soil core sample post-EZVI injection showing EZVI and individual sand grains

Performance assessment activities for the EZVI demonstration included soil and groundwater characterization activities to establish DNAPL distribution and mass, as well as mass flux measurements and the EZVI distribution after the injection. Exhibit 4 shows a microscope photograph of the EZVI adjacent to grains of sand in a soil core sample collected after injection of the EZVI.

Linear interpolation of data from analysis of soil core samples indicated that before EZVI treatment, 17.8 kg of total TCE (both dissolved- and DNAPL-phase TCE) were present in the treatment zone. Of that mass, 3.8 kg were estimated to be present as a separate DNAPL phase. After treatment, the estimated total TCE mass in the plot declined to 2.6 kg, of which 0.6 kg were DNAPL. Linear interpolation indicated that, following treatment with EZVI, the total TCE and DNAPL masses in the plot declined by 86 percent and 84 percent, respectively. A snapshot of TCE groundwater concentrations in shallow wells can be seen in the pre- and postdemonstration TCE concentration contours captured in Exhibit 5.

Krieging of data from analysis of soil core samples indicated that the average total TCE mass in the target zone before EZVI treatment was 28 kg. After treatment, the calculated average total TCE mass was 11.7 kg, indicating a decline in total TCE mass of 58 percent. Only total TCE mass data were subjected to krieging analysis due to the limited number of DNAPL data points available. It is likely that considerably higher degradation of TCE mass may have been achieved had the placement of the EZVI been more uniform in the treatment area. During injection of the EZVI with the pressure pulse technology, a portion of the EZVI migrated upward, and, therefore, little to no EZVI reached some of the targeted depth regions.

The TCE concentrations in groundwater samples from monitoring wells downgradient of the treatment area decreased significantly following EZVI injection (Exhibit 6), resulting in an estimated decrease in mass flux from 1,826 to 810 millimoles per day (mmoles/day). Exhibit 7 shows groundwater concentrations of TCE and TCE degradation products before injection of EZVI (predemonstration), four months after injection (postdemonstration), and 18 months after injection (long-term). Following application of the EZVI, the concentration of TCE degradation products increased substantially, likely due to biological activity. The increase in *cis*-1,2-dichloroethene (cDCE) and vinyl chloride (VC) is believed to be associated with incomplete biodegradation of TCE by

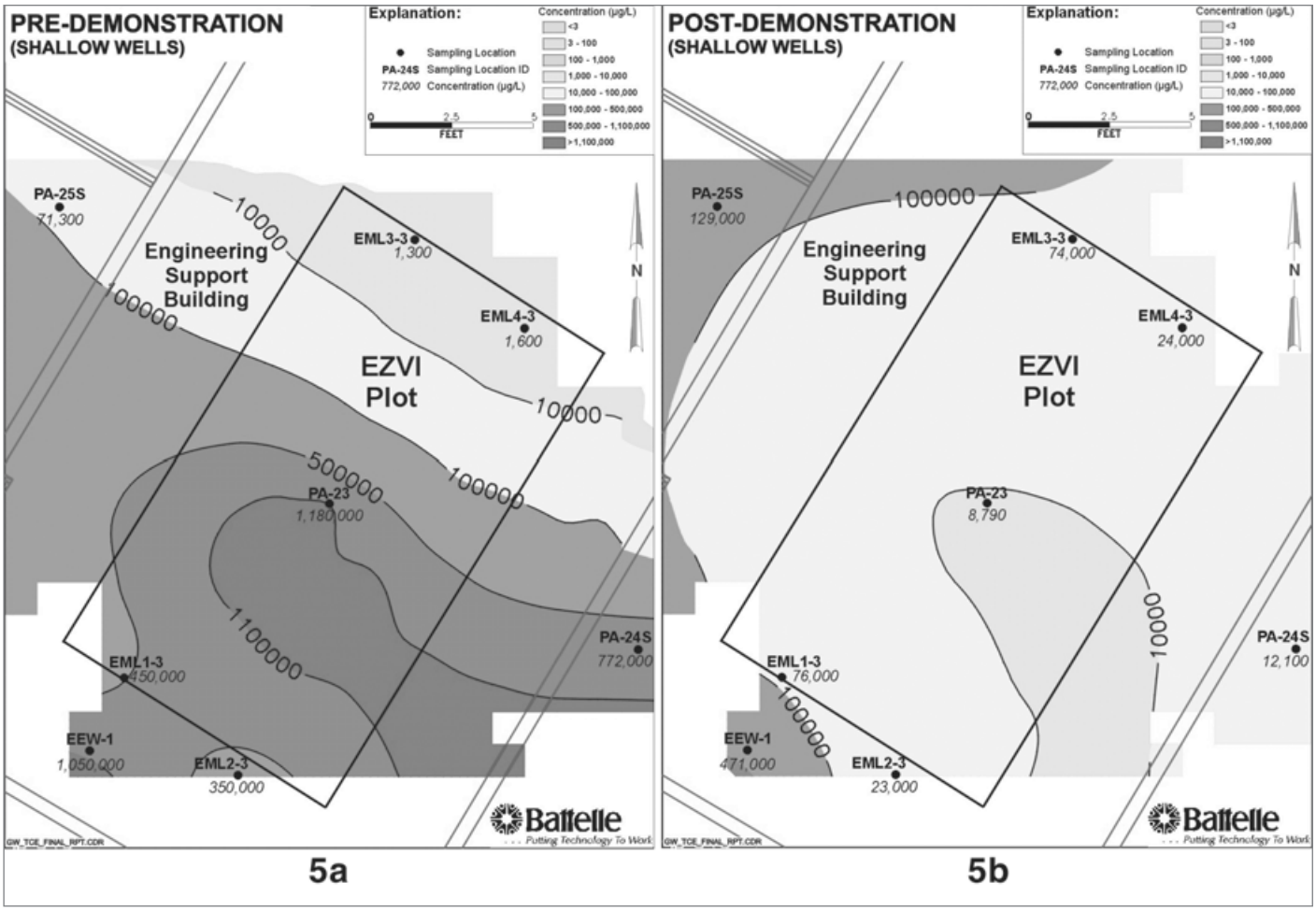

Exhibit 5. Dissolved TCE concentrations in shallow groundwater (µg/L) during (a) predemonstration (March 2002) and (b) post-demonstration (November 2002)

microorganisms present at the site, as these compounds were not observed during testing of the EZVI during sterile lab conditions (Geiger et al., 2003).

Slug tests performed before and after EZVI treatment did not indicate any changes in aquifer permeability. The oxidation-reduction potential (ORP) and dissolved oxygen (DO) decreased slightly after the EZVI treatment, with changes attributable to the anaerobic conditions generated by either the vegetable oil or iron components of EZVI. Groundwater pH remained relatively stable (close to neutral) throughout the demonstration.

Injection Method Evaluation

As a result of the difficulties in obtaining a uniform distribution of the EZVI, a field test was initiated in January 2004 to evaluate alternative delivery methods for EZVI. Four injection technologies were tested: (a) pneumatic fracturing, (b) hydraulic fracturing, (c) pressure pulsing, and (d) direct push injection. The tests were conducted in an open field near the LC34 demonstration site at a depth interval between 16 and 19 feet bgs. One hundred gallons of EZVI made with NZVI were injected at the target depth inter-

	TCE (µg/L)			*cis*-1,2-DCE (µg/L)			Vinyl Chloride (µg/L)		
Well ID	**PreD***	**PostD***	**LT***	**PreD***	**PostD***	**LT***	**PreD***	**PostD***	**LT***
PA-23	1,180,000	8,790	NA	16,900	169,000	NA	<1,000	21,600	NA
EEW-1	1,050,000	471,000	NA	67,100	80,100	NA	<1,000	6,980	NA
EML-1	450,000	76,000	2,700	11,000	96,000	77,900	<500	29,000	33,500
EML-2	350,000	23,000	1,000	21,000	130,000	5,320	<500	20,000	4,950
EML-3	1,300	74,000	740	<100	41,000	2,630	<100	500	1,830
EML-4	1,600	24,000	<100	130	42,000	1,150	<20	1,500	1,460
PA-24S	772,000	12,100	NA	47,400	31,700	NA	<1,000	1,580	NA
PA-25S	71,300	129,000	NA	69,200	42,800	NA	<1,000	75J	NA

Note. NA = not analyzed; PreD = Predemonstration (March 2002); PostD = Postdemonstration (4 months; November 2002); LT = Long-term (18 months; December 2003).

Exhibit 6. TCE, cDCE, and VC concentrations in groundwater from the multilevel wells before and after EZVI injection

val using each of the four injection methods. Following injection, core samples were collected from around each injection location to evaluate the distribution of EZVI using each method. Pneumatic fracturing and direct push emerged as the most promising technologies, allowing for controlled injections without loss of EZVI above or below the targeted interval.

SUMMARY OF LABORATORY DATA FOR EZVI AND ZVI

A laboratory treatability study was conducted in 2005 to evaluate the use of EZVI to treat DNAPL TCE. The objective of the study was to better understand the mechanisms, which contribute to the performance of the technology. It is believed that degradation of chlorinated solvents, such as TCE, following the addition of EZVI occurs as a result of abiotic dechlorination associated with NZVI and enhanced biodegradation occurring as a result of the addition of an electron donor in the form of the oil emulsion. In addition to these degradation mechanisms, TCE concentrations in water will also be reduced as a result of sequestration of the TCE into the oil phase of the EZVI. This sequestration mechanism appears to be very significant in reducing the concentration of TCE immediately following injection of EZVI.

Tests were conducted evaluating the degradation of TCE in the dissolved phase (approximately 1,100 mg/L of TCE in water) and TCE as a DNAPL (approximately ten times greater than saturation concentrations added to the treatment bottles).

Dissolved-Phase Treatability Tests—Summary of Methods

Initial tests were conducted using near-saturation concentrations of TCE in the water. A total of 27 test reactor bottles (9 different treatments, each in triplicate) were constructed on December 14, 2004. All materials required to construct the various test re-

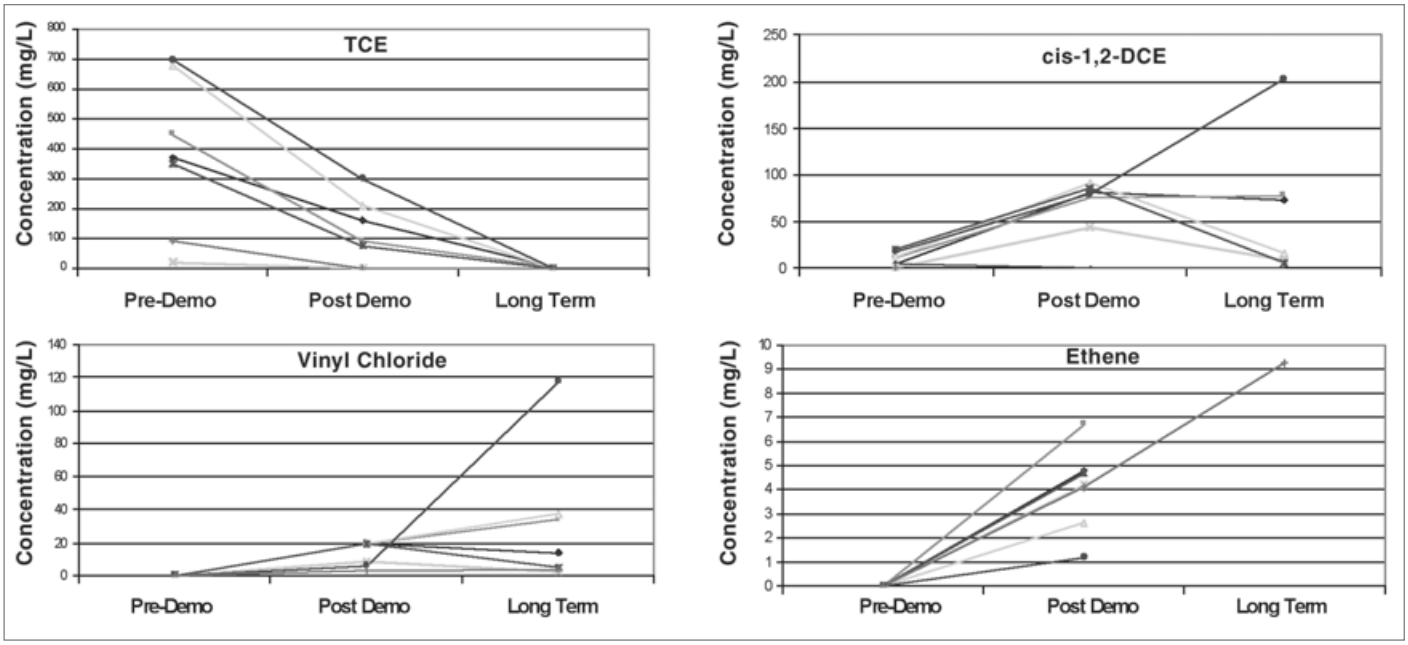

Exhibit 7. TCE, cDCE, VC, and ethene concentrations in monitoring wells within and around the pilot test area before, four months after and 18 months after EZVI injection

actors were placed in an anaerobic glove box. Test reactors were constructed in the glove box by filling 110-mL (nominal volume) glass bottles with 100 mL of anaerobic deionized water. The test reactors were capped with Mininert™ closures to allow repetitive sampling of the bottles with minimal volatile organic compound (VOC) loss. All test reactors were spiked with 72 microliters (µL) of TCE to a target concentration of 1,100 mg/L (0.8 mmol of TCE per bottle). Test reactors were held for 24 hours to allow TCE concentrations in the water and headspace to equilibrate. Following this equilibration period, all test reactors were removed from the glove box and stored at room temperature on an orbital shaker rotating at 150 RPM. The nine different treatments are described below.

Sterile Control Treatment

Test reactors were amended with 1.85 mL of 2.7 percent mercuric chloride (equal to a final liquid concentration of 0.05 percent) to inhibit microbial activity. The test reactors were then bioaugmented with KB-1™, an active bacterial culture known to degrade TCE to ethene under anaerobic conditions, to target concentration of 1×10^8 cells per liter (cells/L). This bacterial culture was added to determine if there were any components in the KB-1™ other than the active microorganisms that would affect the concentrations of the TCE during the test period.

Active Control Treatment

No amendments were added to these test reactors. This treatment was included to evaluate abiotic losses due to sampling and storage and possible biodegradation.

EZVI + KB-1™ Treatment

Test reactors were amended with 6.6 g of EZVI containing 0.636 g of NZVI on a dry weight basis. The amount of EZVI added to the EZVI treatment bottles was calculated based on five times the theoretical amount of NZVI required to degrade the TCE in the test reactor. The test reactors were then bioaugmented with KB-1™ to a target concentration of 1×10^8 cells/L.

The amount of EZVI added to the EZVI treatment bottles was calculated based on five times the theoretical amount of NZVI required to degrade the TCE in the test reactor.

Sterile EZVI + KB-1™ Treatment

Test reactors were amended with 1.85 mL of 2.7 percent mercuric chloride (equal to a final liquid concentration of 0.05 percent) to inhibit microbial activity. The same quantities of EZVI and KB-1™ used in the "EZVI + KB-1™ Treatment" were then added to the test reactors.

Oil Emulsion + KB-1™ Treatment

Test reactors were amended with 6.0 mL of oil emulsion (vegetable oil, surfactant, and water containing no NZVI). The amount of oil emulsion added to this treatment was the same as was used in the EZVI treatment bottles. The test reactors were then bioaugmented with KB-1™ to a target concentration of 1×10^8 cells/L.

Sterile Oil Emulsion + KB-1™ Treatment

Test reactors were amended with 1.85 mL of 2.7 percent mercuric chloride (equal to a final liquid concentration of 0.05 percent) to inhibit microbial activity. The same quantities of oil emulsion and KB-1™ used in the "Oil Emulsion + KB-1™ Treatment" were then added to the test reactors.

ZVI + KB-1™ Treatment

A mass of 1.2 g of NZVI slurry (with a moisture content of 47 percent) was added to the test reactors to provide a mass of 0.636 g of NZVI on a dry weight basis. The test reactors were then bioaugmented with KB-1™ to a target concentration of 1×10^8 cells/L.

Sterile ZVI + KB-1™ Treatment

Test reactors were amended with 1.85 mL of 2.7 percent mercuric chloride (equal to a final liquid concentration of 0.05 percent) to inhibit microbial activity. The same quantities of NZVI and KB-1™ used in the "ZVI + KB-1™ Treatment" were then added to the test reactors.

The deionized water used to construct the test reactors had a pH of approximately 6.5. Monitoring data collected during the initial six weeks showed that the pH of the bottles dropped below levels optimal for growth of the microorganisms in KB-1™. The pH of the biologically active treatments was buffered on Day 54 and on Day 62, and the treatments were re-amended with KB-1™ on Day 62.

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Results from the Different Dissolved-Phase Test Reactors

Exhibit 8 presents a summary of the test reactors' monitoring results following the addition of the amendments described. The amount of TCE and other chlorinated ethenes is presented in terms of mmoles per reactor bottle to allow comparison with the initial loading of TCE into the bottles on a molar basis. The amounts of TCE shown on the graphs in Exhibit 8 are based on the aqueous-phase concentrations and do not include TCE and degradation products that are bound up or sequestered into any oil phase that may be present in the reactor. The results obtained with the sterile and intrinsic control treatments were virtually identical, and only the data from the intrinsic control treatment are shown in Exhibit 8a. As expected, no degradation of the TCE was observed in the controls, and there were no significant losses due to sampling and incubation of the test reactors.

Exhibits 8b and 8c show the results of the dissolved-phase TCE oil emulsion treatments. In the oil emulsion treatments, the TCE in the reactor bottles dropped almost immediately from 0.8 mmol to approximately 0.15 mmol. During the first 50 days of treatment, no by-products of degradation were observed, indicating that the decreases in aqueous concentrations are likely due to the sequestration of the TCE into the vegetable oil. After the pH was buffered and the test reactors were re-amended with KB-1™ on Day 62, the concentrations of TCE started to increase in the active (i.e., not sterilized) oil emulsion treatment (Exhibit 8b), and some TCE was being degraded to *cis*-1,2-dichloroethene (cDCE). The increase in TCE concentrations may have been due to bacteria breaking down the vegetable oil and releasing some of the sequestered TCE into the water. Although there was some conversion of the TCE to cDCE, KB-1™ does not appear to have been able to degrade the TCE to ethane, likely as a result of the use of deionized water to construct the test reactors rather than natural groundwater. Micronutrients and additional microorganisms that may assist in breaking down the vegetable oil into a usable electron donor exist in natural groundwater, and their absence in the test reactors likely limited the extent of biodegradation.

Exhibits 8d and 8e show the results of the NZVI treatments. There were no significant differences between the sterile and active NZVI treatments, indicating that the dominant degradation mechanism in these test reactors was abiotic degradation associated with the NZVI. The TCE concentrations dropped rapidly, from 0.8 mmol down to 0.17 mmol within the first day. After the first seven days, very low quantities of TCE persisted in the NZVI treatment test reactors. The concentrations of TCE decreased from an average of 0.009 mmol to 0.001 mmol on Day 63, until Day 69 when TCE was nondetect. Trace amounts of cDCE and vinyl chloride were detected in the samples, but the data show that most of the TCE was converted to nonchlorinated end products such as ethene and ethane. Due to analytical constraints, the only gases that were analyzed were ethene and ethane, although it is expected that other C2 and C4 gases are being produced (e.g., acetylene, butane, 1-butylene) and may account for the decrease in total ethenes and ethane (Liu et al., 2005).

The decrease in TCE in the NZVI treatment was accompanied by a rapid increase in the chloride concentrations from approximately 2 mg/L to 942 mg/L by Day 8 in the active NZVI treatment.

The decrease in TCE in the NZVI treatment was accompanied by a rapid increase in the chloride concentrations from approximately 2 mg/L to 942 mg/L by Day 8 in the active NZVI treatment (Exhibit 9). The chloride concentrations varied between 722 mg/L and just over 900 mg/L for the remainder of the test. The TCE added to the reactors (0.8 mmol) could produce 85 mg of chloride if it were completely degraded (0.8 mmol of TCE times

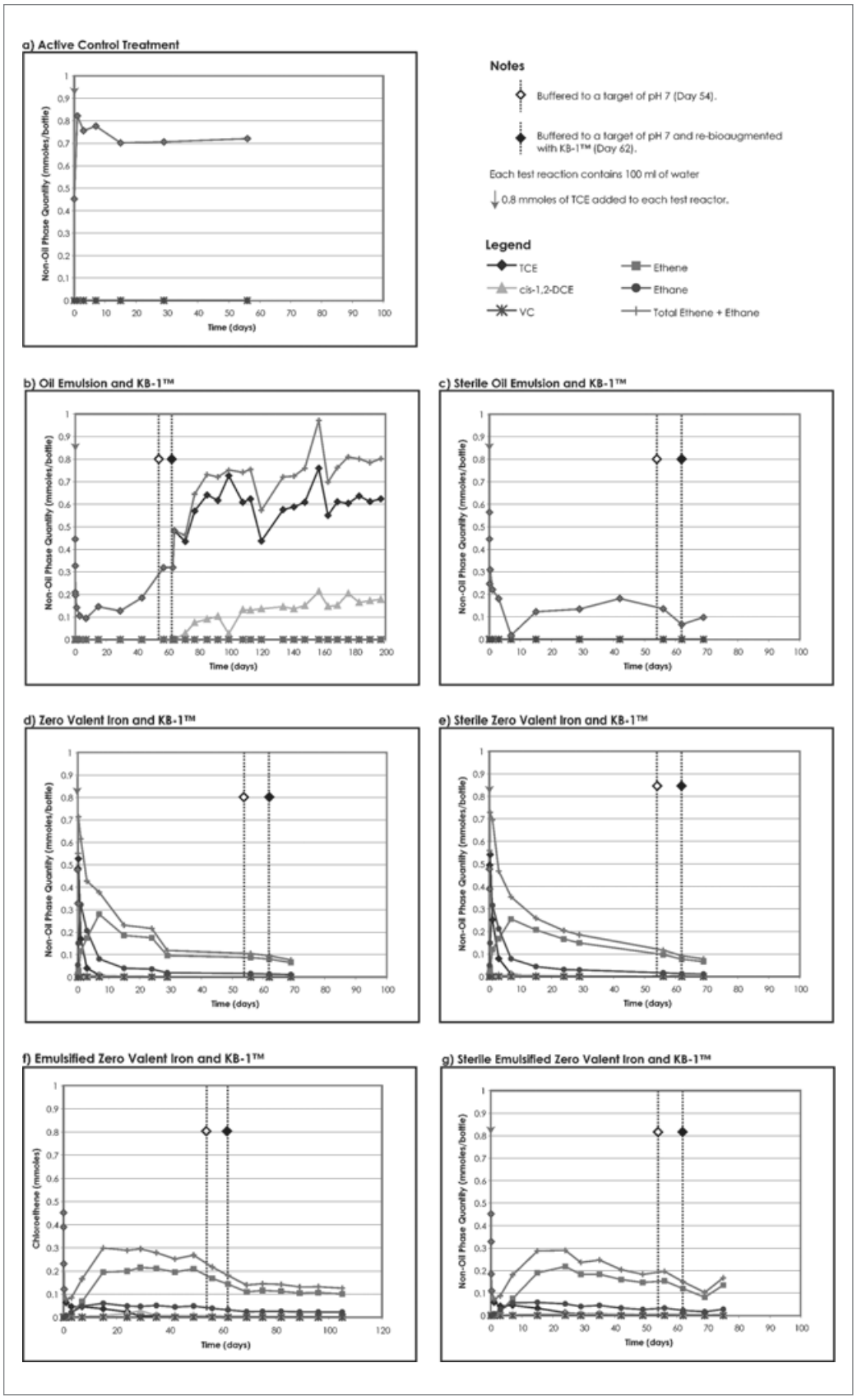

Exhibit 8. Summary of results of dissolved-phase TCE laboratory treatments

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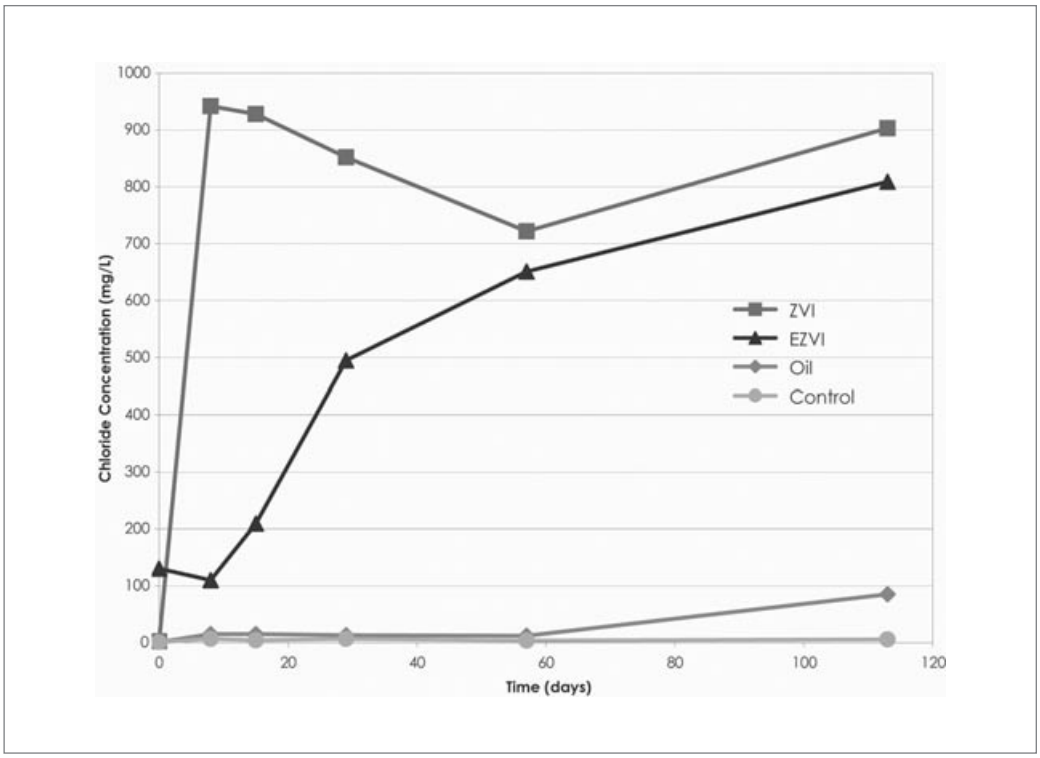

Exhibit 9. Aqueous chloride concentrations in dissolved-phase TCE laboratory treatments

106.35 mg of chlorine per mmol of TCE). The 85 mg in the 100-mL bottles would be expected to produce a maximum aqueous phase concentration of 850 mg/L of chloride in the bottles. The measured concentrations of chloride between 722 and 942 mg/L demonstrated there was virtually complete degradation of the TCE in the ZVI treatment.

Exhibits 8f and 8g show the results of the EZVI treatments. The results obtained with both the sterile and active EZVI treatments were very similar, indicating that the decreases in the quantities of TCE observed were due to the ZVI and sequestration into the oil emulsion and not due to biological activity. In these treatments, the quantity of TCE dropped almost immediately from 0.8 mmol down to 0.06 mmol. This initial drop is likely due to a combination of the sequestration of the TCE into the vegetable oil and the degradation of the TCE by the NZVI in the EZVI. Other than small quantities of cDCE and trace amounts of VC, the main degradation products observed in the EZVI treatments were ethene and ethane. At Day 57, two of the EZVI test reactors were sacrificed to determine the quantities of VOCs partitioned into the oil phase of the emulsion droplets. The oil phase from these test reactors contained an average of 0.0128 mmol of chlorinated ethenes (0.0034 mmol of TCE and 0.0094 mmol of cDCE). The initial loading of TCE to each of the reactors was 0.8 mmol, and 0.01 mmol of chlorinated ethenes were present in the water when the oil-phase samples were taken. These data suggest that 98 percent of the TCE initially added to the bottles was converted to nonchlorinated end products in the EZVI treatments. By Day 77, TCE was not detected in the water in either the sterile or active test reactors.

As with the NZVI treatments, the decrease in TCE in the EZVI treatments was accompanied by an increase in the chloride concentrations in the aqueous phase; however,

in the EZVI treatments, the increase in chloride concentrations took place gradually over the experiment (Exhibit 9). The final chloride concentration at 113 days was 809 mg/L. As discussed earlier, the TCE added to the reactors would be expected to produce a concentration of 850 mg/L of chloride in the aqueous phase. The chloride concentration in the EZVI test increased slowly and was likely still increasing when it reached 809 mg/L at 113 days. These data demonstrate that the TCE in the EZVI treatment is degraded and not just sequestered in the oil. The slow increase in chloride may be due to slow degradation of the TCE or slow diffusion of the chloride out of the emulsion following dechlorination of the TCE. The measured concentration of chloride of 809 mg/L at Day 113 demonstrates there was degradation of at least 95 percent of the TCE in the EZVI treatment. This may be an underestimate of the amount of degradation if there was residual chloride still in the emulsion at the time the sample was collected that was not measured in the aqueous-phase sample.

All three treatments—oil emulsion, NZVI, and EZVI—showed significant and rapid decreases in TCE relative to the active control.

Comparison of the Dissolved-Phase Test Reactors

All three treatments—oil emulsion, NZVI, and EZVI—showed significant and rapid decreases in TCE relative to the active control. The decrease in TCE in the oil emulsion treatment is believed to be due to sequestration of the TCE into the oil, as there was little production of chloride. The decrease in the quantity of TCE in the NZVI treatment was accompanied by an increase in the aqueous-phase concentration of chloride, demonstrating that complete degradation of the TCE was achieved in a very short period of time. The results were virtually identical for the active and the sterile NZVI treatments, demonstrating that the degradation is due to abiotic degradation of the TCE resulting from the NZVI. The rapid decrease in TCE in the EZVI treatment is believed to be due to a combination of both sequestration and abiotic degradation. The decrease in the quantity of TCE in the EZVI treatment was followed by a slow increase in the aqueous-phase concentration of chloride, demonstrating that complete degradation of the initial spike of TCE was eventually achieved.

Based on the early-time data it appears that the NZVI alone provides a more rapid degradation than the EZVI, but the late-time data indicate that the extent of degradation is very similar between the two treatments. The results of the testing suggest that the EZVI provides for complete degradation of the TCE in a time frame similar to that obtained with the NZVI and also provides sequestration of any potential untreated VOCs as well as electron donors for follow-on biodegradation of potential untreated VOCs.

DNAPL Treatability Tests—Summary of Methods

Additional laboratory tests were conducted to evaluate the degradation of DNAPL TCE in the presence of EZVI and the components of EZVI. A total of 12 test reactors (4 treatments in triplicate) were constructed for the DNAPL treatability tests. Active DNAPL controls and NZVI DNAPL treatments were constructed by filling 250-mL (nominal volume) glass bottles with 200 mL of purified anaerobic water. EZVI DNAPL treatments and oil emulsion DNAPL treatments were constructed by filling 250-mL glass bottles with 150 mL of purified anaerobic water. The test reactors were capped with Mininert™ closures to allow repetitive sampling of the bottles with minimal VOC loss. All test reactors were spiked with 1.5 mL of TCE to an initial loading

of 16.7 mmol per bottle of TCE, an amount equal to approximately ten times saturation concentrations.

The test reactors were constructed in triplicate and allowed to incubate for 72 hours to allow the TCE DNAPL to dissolve into the aqueous phase and reach the equilibrium concentrations. The amount of EZVI added to the EZVI treatment bottles was calculated based on two times the theoretical amount of ZVI required to degrade the TCE in the test reactor. The amounts of NZVI and oil added to the NZVI and oil emulsion treatments were the same as were used in the EZVI treatment bottles. Test reactors were stored in the anaerobic glove box over the test period. The results of the dissolved-phase treatment tests demonstrated very little difference in the results obtained with the active and sterile variations of the different treatment tests. As a result, all DNAPL treatments were active treatment (no mercuric chloride added). The specific details for the construction of the different treatments after the initial incubation are described below.

Active DNAPL Control Treatment

No amendments were made to these test reactors. Test reactors were used to evaluate abiotic losses due to sampling and incubation and biotic losses related to the groundwater.

Oil Emulsion DNAPL Treatment

A total of 50 mL of emulsion (with no ZVI) was added into each of the reactor. The test reactors were bioaugmented with KB-1™ to a target concentration of 1×10^8 cells/L. Test reactors were used to evaluate biologic degradation due to electron donors (oil and surfactant) and the amount of sequestering in the oil phase.

ZVI DNAPL Treatment

A mass of 10.5 g of Toda NZVI (RNIP-10DS) was added to each of the reactors. The test reactors were then bioaugmented with KB-1™ to a target concentration of 1×10^8 cells/L. Test reactors were used to evaluate abiotic degradation due to ZVI.

The results of the dissolved-phase treatment tests demonstrated very little difference in the results obtained with the active and sterile variations of the different treatment tests.

EZVI DNAPL Treatment

A total of 56 g of EZVI (containing the same amount of NZVI [10.5 g] as the ZVI treatments and the same amount of vegetable oil and surfactant as the emulsion treatments) was added to each test reactor. The test reactors were then bioaugmented with KB-1™ to a target concentration of 1×10^8 cells/L. Test reactors were used to evaluate abiotic and potential biologic degradation due to EZVI.

Results of the DNAPL Test Reactors

Exhibit 10 presents a summary of the test reactors' monitoring results following the addition of the amendments described. The amount of TCE and other chlorinated ethenes is presented in terms of mmol per reactor bottle to allow comparison with the initial loading of TCE into the bottles on a molar basis (16.7 mmol per bottle). The amounts of TCE shown on the graphs in Exhibit 10 are based on the aqueous-phase concentrations

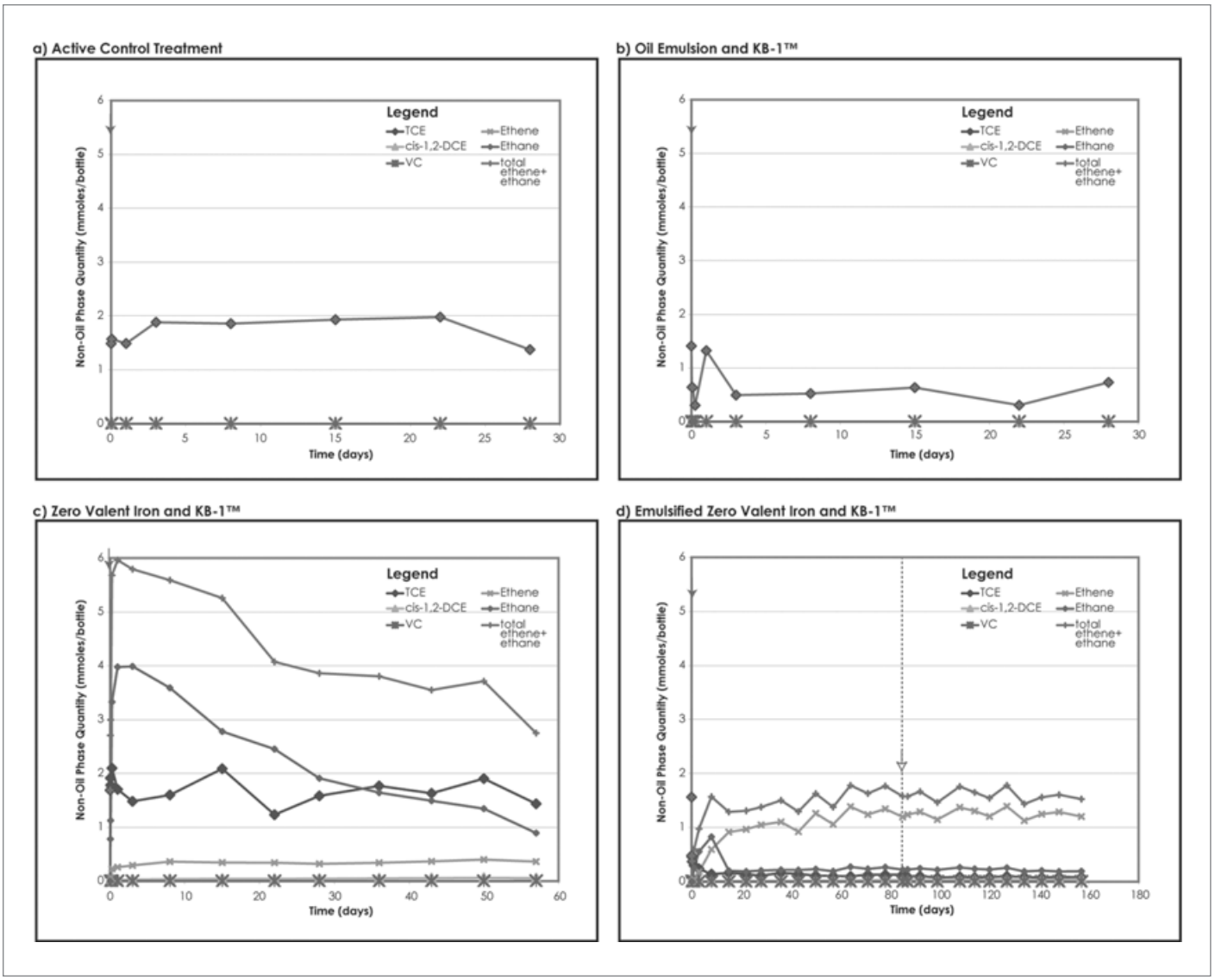

Exhibit 10. Summary of results of DNAPL-phase TCE laboratory treatments

and do not include TCE and degradation products that are bound up or sequestered into any oil phase or into any DNAPL phase that may be present in the reactor.

Exhibit 10a shows the results of the intrinsic control treatment. As expected, no degradation of the TCE occurred in the controls, and there were no significant losses due to sampling and incubation of the test reactors.

In the oil emulsion treatments (emulsion without the NZVI; Exhibit 10b), the TCE concentration dropped almost immediately from 16.7 mmol to approximately 0.57 mmol. This immediate drop in concentration is believed to be due to the sequestration of the TCE into the oil phase of the emulsion. Based on the results of the dissolved-phase treatments, it was believed that biodegradation would not be significant in these DNAPL tests using the deionized water, and sampling was stopped after Day 27. Although there is some variability in the TCE concentrations measured in the water phase, no degradation products were observed. On Day 27, the moles of TCE in the aqueous phase had

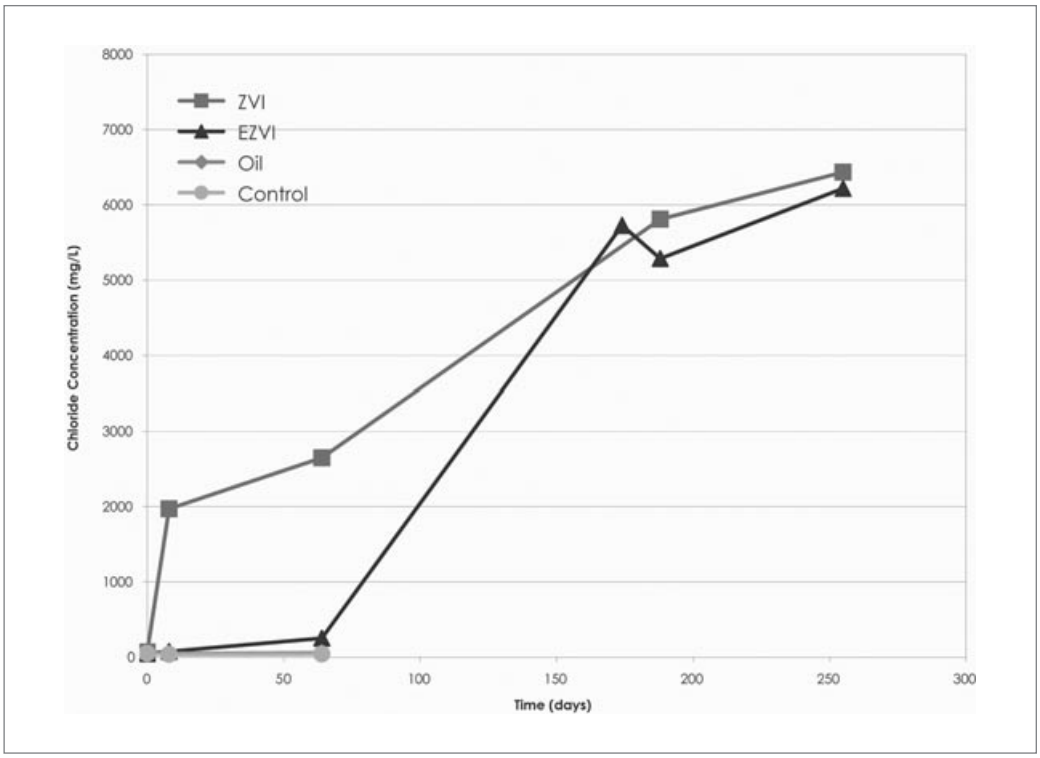

Exhibit 11. Aqueous chloride concentrations in DNAPL-phase TCE laboratory treatments

dropped from the initial loading of 16.7 mmol to 0.29 mmol due to the sequestration of the DNAPL into the vegetable oil emulsion. Since the oil emulsion treatments have no ZVI, they are composed solely of water, surfactant, and vegetable oil. The oil emulsion is therefore a light nonaqueous phase liquid (LNAPL) that floats on the top of the water. As the TCE DNAPL combined with the oil emulsion, a portion of the emulsion became denser than water and settled to the bottom of the bottle as a DNAPL. On Day 27, a separate DNAPL phase could still be observed in the vial.

Exhibit 10c shows the results of the NZVI treatments. The amount of TCE measured in the water in the reactor bottles throughout the duration of the test ranged between 1.2 and 2.0 mmol per bottle, close to the saturation concentration of TCE of 1.67 mmol per bottle. The amount of TCE measured in the aqueous phase in the bottles corresponds to the amount that would be expected to be observed in water in the presence of TCE DNAPL. There was an increase in the amount of ethane at the start of the test (up to 4 mmol per bottle) and small amounts of ethene and cDCE. The gradual decline in the total ethenes and ethane is likely due to the natural degradation of nonchlorinated ethane and ethene or due to losses of these volatile gases during sampling.

In the NZVI treatments, there was an increase in the aqueous chloride concentration from 68 mg/L at time 0 to 1,970 mg/L at Day 8; 2,650 mg/L at Day 64; and 5,800 mg/L at Day 188 (Exhibit 11). The TCE added to the reactors (16.7 mmol) could produce a maximum of 1,776 mg of chloride if it were completely degraded (16.7 mmol of TCE times 106.35 mg of chlorine per mmol of TCE). The 1,776 mg in the 200 mL of water in the bottles would produce an aqueous-phase concentration of 8,880 mg/L of chloride. The measured aqueous-phase concentrations of chloride up to 6,434 mg/L

demonstrate there was degradation of approximately 67 percent of the TCE at Day 255 in the NZVI treatment. The TCE concentration in the NZVI bottles was stable at about the saturation concentration from about three days up to the last sampling event for chlorinated ethenes at Day 63. During the test, a dense material believed to contain residual iron particles and TCE DNAPL was present in the bottom of the bottles. The data and observations suggest that the NZVI alone was capable of degrading at least 73 percent of the original mass of TCE DNAPL but that the aqueous concentration of TCE remained at saturation concentrations because of the presence of residual TCE DNAPL.

Exhibit 10d shows the results of the EZVI DNAPL-phase treatments. In the EZVI treatments, the amount of NZVI in the EZVI added to the test reactors was exactly the same as that added to the NZVI treatments. In the EZVI treatment, the quantity of TCE in the nonoil phase decreased almost immediately down to 0.18 mmol by the end of the first day. The quantity of TCE after Day 1 was much lower in the EZVI treatments than in the NZVI due to the additional benefit of the sequestration of the TCE into the oil phase. As in the NZVI treatments, there was an initial increase in ethane, but it quickly switched to ethene production. Very low quantities of cDCE were measured and no VC was observed. In the EZVI treatments, there was little increase in the chloride concentration from the start of the test to Day 64 (Exhibit 11).

The measured concentration of chloride in the water of 6,218 mg/L demonstrates there was degradation of at least 71 percent of the TCE at Day 255 in the EZVI treatment.

At Day 157, two of the EZVI test reactors were sacrificed to determine the quantity of chlorinated ethenes partitioned into the oil phase of the emulsion droplets. The oil phase from these test reactors was found to have an average of 2.94 mmol of chlorinated ethenes (2.68 mmol of TCE and 0.26 mmol of cDCE). The initial loading of TCE to each of the reactors was 16.7 mmol, and an additional 0.8 mmol was added at Day 85, for a total of 17.5 mmoles. Based on sampling of the aqueous phase in the test reactors on Day 157, 0.173 mmol of chlorinated ethenes were present in the water when the oil-phase samples were taken. These data suggest that 82 percent of the TCE added to the bottles was converted to nonchlorinated end products in the EZVI treatments by Day 157 of the test.

In the EZVI treatments, there was little increase in the chloride concentration from the start of the test to Day 64 (Exhibit 11). The concentration, however, increased significantly to 6,218 mg/L after 255 days. As discussed earlier, the TCE added to the reactors initially could produce a concentration of 8,880 mg/L of chloride in the water in the sample bottles. The EZVI treatment bottles were respiked with TCE after 85 days such that the concentration of chloride would be 9,305 mg/L if all the TCE were to be degraded. The measured concentration of chloride in the water of 6,218 mg/L demonstrates there was degradation of at least 71 percent of the TCE at Day 255 in the EZVI treatment. As discussed earlier, analysis of the oil and water at 157 days showed that 82 percent of the TCE was degraded. Analysis was not performed to determine the amount of chloride present in the oil phase in the reactor bottles. It is believed that a significant proportion of the missing chloride mass may have been present as inorganic chloride in the EZVI.

Comparison of the DNAPL Phase Reactors

The results of the DNAPL treatments demonstrated significant differences between the performances of the three different treatments (oil emulsion, NZVI, and EZVI). As in the dissolved-phase treatments, the oil emulsion treatment quickly reduced the aqueous-

phase concentration of TCE to less than the solubility of TCE in water, but a residual concentration of 200 to 400 mg/L of TCE remained in the aqueous phase for the duration of the DNAPL test. These results are believed to be primarily due to sequestering the TCE into the oil phase, as no degradation products were observed in these reactors. In the NZVI treatments, the concentration of the TCE dropped to near the saturation concentration of about 1,100 mg/L within the first day, but no further decreases in TCE concentrations were observed after 55 days. The production of ethane, ethane, and chloride indicates that significant degradation of the TCE was occurring as a result of the NZVI, but this degradation did not result in a decrease in the aqueous-phase concentrations below the saturation concentration during the test. The EZVI treatments showed the most promising results, with concentrations of TCE decreasing within a few hours to about 300 mg/L (30 percent of the saturation concentration of TCE) then decreasing to about 100 mg/L (10 percent of the saturation concentration) within about a week. The production of ethene and eventual production of chloride indicated that the TCE was being degraded by the NZVI within the EZVI. Treatment with EZVI benefits from both the sequestration of the TCE by the oil phase and degradation due to the NZVI.

These DNAPL treatment tests demonstrate the advantages of EZVI over straight vegetable oil addition or NZVI alone in situations where a DNAPL is present in the subsurface. The EZVI combines the sequestration of the DNAPL with the degradation of the VOCs by the NZVI resulting in an immediate reduction in the TCE flux from the source area as well as degradation due to the NZVI. As an added benefit, the addition of an electron donor (vegetable oil) can enhance biodegradation of any potential untreated chlorinated ethenes should appropriate dehalorespiring bacteria exist at the site.

SUMMARY AND CONCLUSIONS

The results of the first field-scale injection of EZVI at the LC34 demonstration site indicate that significant reductions in groundwater TCE concentrations (57 percent to 100 percent) were obtained at all depths targeted with EZVI within five months. It is believed that the reductions in TCE concentrations would have been even greater if the distribution of the EZVI had been more uniform. Significant additional decreases in TCE were observed in long-term groundwater samples collected 18 months after the injection of the EZVI. The data suggest that a significant portion of the longer-term decrease in TCE concentrations is due to biodegradation processes enhanced by the presence of the oil and surfactant in the EZVI emulsion. Additional fieldwork conducted after the first field deployment of EZVI demonstrated that significantly improved distribution of the EZVI could be achieved using a pneumatic fracturing injection method or direct push method rather than the pressure pulse technology.

Oil emulsion, NZVI, and EZVI treatment of dissolved-phase TCE can produce significant and rapid decreases in TCE concentrations in the aqueous phase.

The laboratory study provided valuable insight into the mechanisms responsible for decreases in TCE concentrations with the application of EZVI. The key findings of the laboratory study are as follows:

1. Oil emulsion, NZVI, and EZVI treatment of dissolved-phase TCE can produce significant and rapid decreases in TCE concentrations in the aqueous phase. The data for the laboratory tests suggest that the decrease in TCE in the oil emulsion treatment is due to sequestration of the TCE into the oil; in the NZVI treatment, it is due to abiotic degradation of the TCE associated with the NZVI; and in the

EZVI treatment, it is due to a combination of both sequestration and abiotic degradation. Biological degradation of dissolved-phase TCE was not significant in any of the different treatments as a result of nutrient-deficient test conditions.

2. Oil emulsion treatment of TCE DNAPL reduced the aqueous-phase concentration of TCE to less than the solubility of TCE in water; however, a significant residual concentration of TCE (e.g., 200 to 400 mg/L versus a solubility of 1,100 mg/L) remained in the aqueous phase. The significant residual concentration of TCE in the aqueous phase is a result of the high loading of TCE in the nonaqueous phase mixture of TCE and oil. The data for the laboratory tests suggest that the decrease in TCE is due to sequestering the TCE into the oil phase only and that there was little or no decrease in the quantity of TCE.
3. NZVI treatment of TCE DNAPL was not able to reduce aqueous concentrations below the saturation concentration of about 1,100 mg/L. The production of ethane, ethene, and chloride indicates that significant degradation of the TCE was occurring as a result of the NZVI, but this degradation did not result in a decrease of the aqueous-phase concentrations below the saturation concentration during the test. The concentration of chloride measured in the aqueous phase after 188 days demonstrated that 73 percent of the original mass of TCE DNAPL was degraded.
4. EZVI treatment of TCE DNAPL was able to reduce concentrations of TCE to about 100 mg/L (10 percent of the saturation concentration) within a week after treatment. The production of ethene and eventual production of chloride indicates that the TCE is being degraded by the NZVI in the EZVI. The reduction in TCE is believed to be from both the sequestration of the TCE by the oil phase and degradation due to the NZVI. Analysis of the oil phase and water phase suggests that 82 percent of the original TCE DNAPL added to the treatment bottle was degraded at Day 157. The concentration of chloride measured in the aqueous phase after 255 days demonstrated that at least 67 percent of the original mass of TCE DNAPL was degraded. The discrepancy between the estimate of the percentage of mass degraded from chlorinated ethene and chloride analysis may be a result of additional chloride trapped in the EZVI, which was not detected in the aqueous-phase analysis.
5. The DNAPL treatment tests demonstrate the advantages of EZVI over oil emulsions or NZVI in situation where a DNAPL is present in the subsurface. The EZVI combines the sequestration of the DNAPL with the degradation of the VOCs by the NZVI resulting in an immediate reduction in the TCE flux from the source area as well as degradation due to the NZVI. The EZVI provides degradation of the TCE to ethene in a similar time frame as the NZVI and also provides sequestration of any potential untreated VOCs.
6. The EZVI provides oil that should be able to act as an electron donor to promote biodegradation of TCE, which is not degraded by the NZVI. The potential beneficial effects of this biodegradation were not observed to a significant degree in the laboratory tests conducted to date, likely because site groundwater and soil were not used in the test reactors.

The DNAPL treatment tests demonstrate the advantages of EZVI over oil emulsions or NZVI in situation where a DNAPL is present in the subsurface.

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