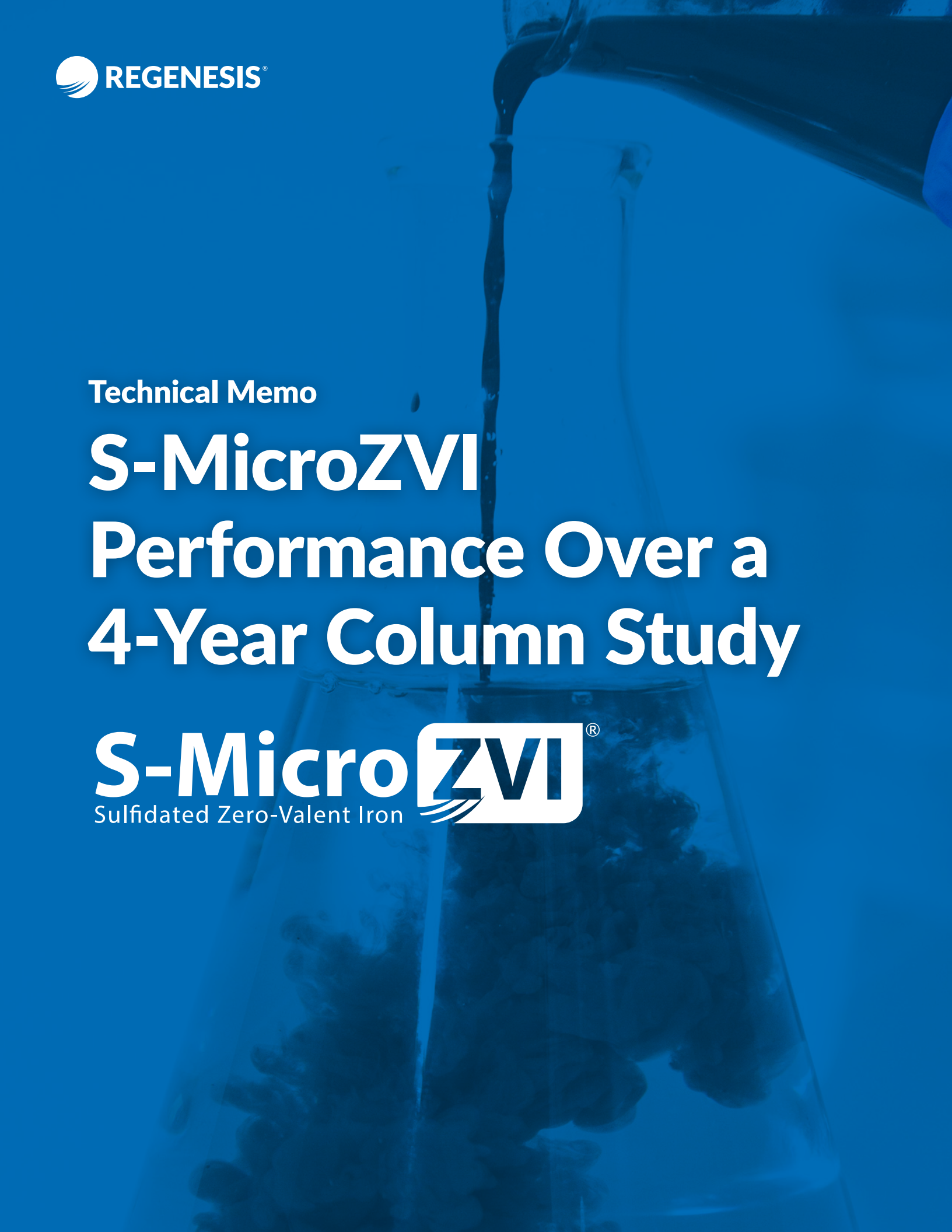
REGENESIS®

Technical Memo

# S-MicroZVI Performance Over a 4-Year Column Study

S-MicroZVI®
Sulfidated Zero-Valent Iron



# Study Overview

Expanding upon previous studies, ISCR-Enhanced Bioremediation[2] and Zero-Valent Iron Technical Bulletin Benefits of Sulfidation,[3] a soil column study was performed to evaluate the longevity of S-MicroZVI. This study was designed to simulate the remediation of a chlorinated ethenes plume passing through a permeable reactive barrier. Over the course of the experiment, dissolved phase trichloroethene was continually passed through sand columns that were:

1. Sterile and untreated (control)
2. Bioaugmented
3. Sterile and treated with S-MicroZVI
4. Bioaugmented and treated with S-MicroZVI

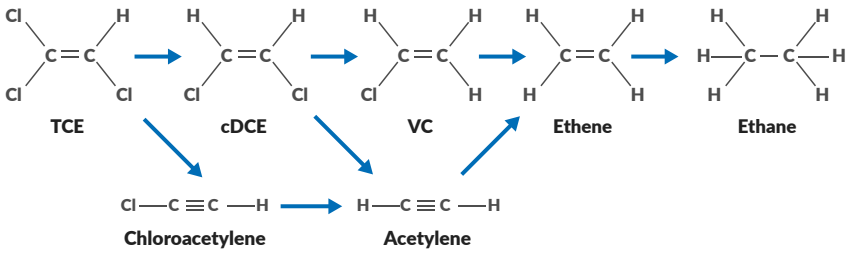
Treatment efficiency was evaluated by measuring concentrations of TCE and the daughter products cis-dichloroethylene and vinyl chloride (cDCE and VC) in the effluent of each column. Initially, a 2 mg/L TCE solution in deoxygenated water was used and as the experiment progressed, the influent was increased to 20 mg/L TCE with 100% dissolved oxygen (DO) saturation to better understand the capabilities of the product. Even after stressing the system, no significant breakthrough of TCE or daughter products was observed until the end of the 4-year experiment; verifying the exceptional reactivity and persistence provided by sulfidated zero valent iron.

# About S-MicroZVI

S-MicroZVI® (sulfidated micro zero-valent iron) is an *in situ* remediation product capable of removing toxic groundwater contaminants via direct chemical reduction reactions. Target contaminants include chlorinated ethenes, Figure 1 chloroalkanes (e.g., 1,1,1-TCA), chloromethanes (e.g., CT), select pesticides and herbicides, and inorganics such as chromium and arsenic.

## Figure 1 Dechlorination Pathways

Diagram showing the reductive dechlorination (upper pathway) or beta-elimination (lower pathway) of chlorinated contaminants.





The small particle size (<5 µm) allows this product to be diluted in water and injected directly into the areas of contamination, avoiding the need to use aggressive product application methods (e.g., fracturing, soil mixing). Another key feature of S-MicroZVI is its core shell configuration with an interior consisting of zero valent iron and a surface layer consisting of reduced iron sulfide (mackinawite). The sulfidated surface effectively inhibits the hydrolysis reaction of ZVI and water and enables the preferential reduction of contaminants. Together these result in improved longevity compared to bare, unsulfidated ZVI products. Sulfidation also increases reaction kinetics by over an order of magnitude for several groundwater contaminants including chlorinated ethenes such as Trichloroethylene (TCE) as summarized by Fan, et al.[1]

# Experimental

## Column Set-up (October 2018)

4 Omnifit columns were assembled utilizing standard methods. All columns were packed from bottom to top with: glass wool, 10 g silica 20 mesh sand, 315 g #60 mesh sand, 10 g silica 20 mesh sand, and glass wool. Prior to adding water or amendments, columns were then flushed with $CO_2$ for 15 minutes.

## The columns were then labeled:

1. Control
2. Bioaugmented
3. S-MicroZVI
4. Bioaugmented/S-MicroZVI

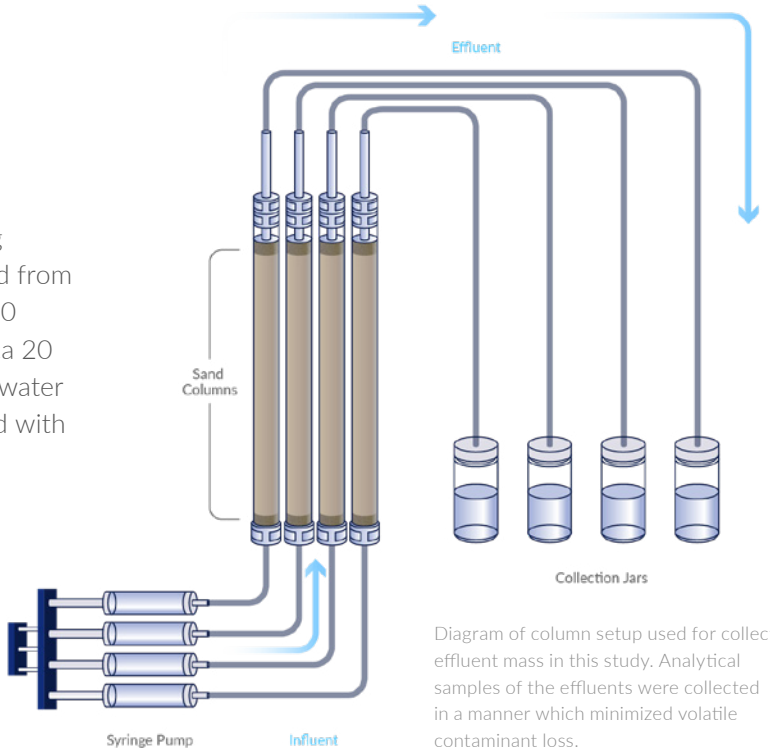



Diagram of column setup used for collecting effluent mass in this study. Analytical samples of the effluents were collected in a manner which minimized volatile contaminant loss.

## The columns were prepared using the following procedures:

1. The sterile and untreated control column was filled with tap water using a peristaltic pump at 5 mL/min.

2. The bioaugmented column was pre-filled with argon-sparged tap water using a peristaltic pump at 5 mL/min. Subsequently, three pore volumes of a mixture of soluble bioremediation amendments (1000 mg/L sodium lactate and 10 mg/L phosphorous and nitrogen nutrients) were flowed through the columns with $10^9$ cells/L of an anaerobic culture containing dehalococcoides added for the last 1.5-2 pore volumes.

3. The S-MicroZVI column was pre-filled with argon-sparged tap water using a peristaltic pump at 5 mL/min. Three pore volumes of an argon sparged 10,000 mg/L S-MicroZVI suspension was then pumped into the column at 8 mL/min. Influent samples were taken at the beginning and end of the application to determine the amount of S-MicroZVI that was deposited within the soil column.

4. The bioaugmented/S-MicroZVI column was assembled using the procedure for the bioaugmented column followed by the procedure for the S-MicroZVI column. Influent and effluent samples were taken to determine the amount of S-MicroZVI that was deposited on the soil column.

# Initial Column Influent Conditions

The flow rate was set at 0.563 mL/hr. (about 1 pore volume/7 days). Influent for control and S-MicroZVI columns started as 2 mg/L TCE in tap water. Before adding TCE, dissolved oxygen (DO) was removed by sparging in tap water with argon. Influent for bioaugmented and bioaugmented/S-MicroZVI columns started as 2 mg/L TCE, 100 mg/L sodium lactate, 1 mg/L nutrients composed of phosphates and ammonia sulfate in Ar-sparged tap water pH adjusted as needed to 7.

## Figure 2 - Experimental Schedule 10/30/2018 – 11/01/2022

Key points in the experiment, including start and end points for each column and concentrations of TCE and DO as the experiment progressed. Fully oxygenated water is assumed to contain about 8 mg/L dissolved oxygen.

| Month | Influent TCE | Oxygenation | Notes |
|---|---|---|---|
| 0 | 2 mg/L | 0% | Experiment started |
| 7.2 | 2 mg/L | 0% | Bioaugmented columns taken down |
| 7.7 | 2 mg/L | 0% | Bioaugmented columns extracted, influent rate 0.268 mL/hr. |
| 12.5 | 5 mg/L | 50% | - |
| 18.6 | 10 mg/L | 50% | - |
| 23.5 | 10 mg/L | 100% | - |
| 35.3 | 20 mg/L | 100% | - |
| 48.1 | 20 mg/L | 100% | S-MicroZVI and Control columns taken down |
| 48.2 | - | - | S-MicroZVI and Control columns extracted |

Effluent composition was measured from collected samples using a GCMS headspace method. The bioaugmented and bioaugmented/S-MicroZVI columns were maintained at the specified conditions for 7 months before they were taken down and extracted to find contamination remaining on soil. The S-MicroZVI and sterile control columns were continued with influent conditions modified as shown in Figure 2.

# Results and Discussion

## Control Column

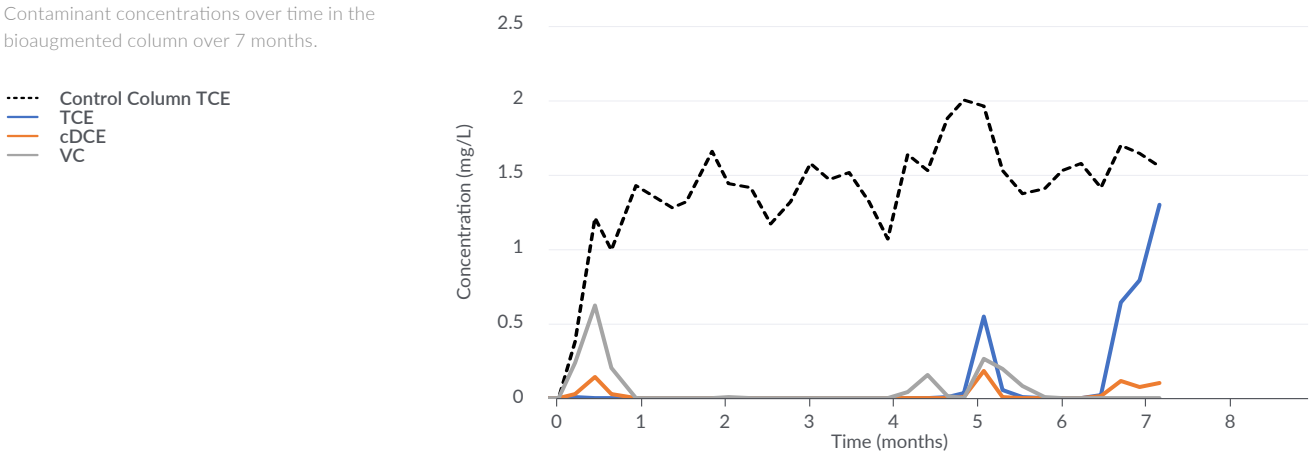
The condition of the control column over 4 years can be seen as an inset of Figures 3-5. This column contained no remediation amendments and as expected, the effluent equilibrated at concentrations averaging about 80% of the influent concentrations. Also, as expected, no daughter products were detected in the effluent. This column verified that the experimental procedure could evaluate the performance of the remediation amendments in a long-term column study. At the conclusion of the soil column experiment, the column was extracted, cDCE was non-detect, TCE on soil was 0.2 mg/kg or less.

## Bioaugmented Column

The performance of the bioaugmented column over 7 months is provided in Figure 3. This column showed degradation of TCE to the daughter products cDCE and VC. In the early stages of the column study (<1 month) VC eluted at concentrations just over 0.6 mg/L or about 30% of the influent TCE on a molar basis. At 4-5 months the column exhibited breakthrough of TCE at concentrations over 0.5 mg/L and daughter products vinyl chloride at concentrations of almost 0.3 mg/L and cDCE at concentrations of almost 0.2 mg/L. At the end of the bioaugmented column study, TCE was eluting at 1.3 mg/L, or 85% of the sterile column TCE elution at the time. After the course of the biotic column experiment, the biotic columns were extracted and analyzed for remaining CVOC mass. Low levels (sub mg/kg) of TCE and cDCE were detectible.

**Figure 3** **Bioaugmented Column**

Contaminant concentrations over time in the bioaugmented column over 7 months.

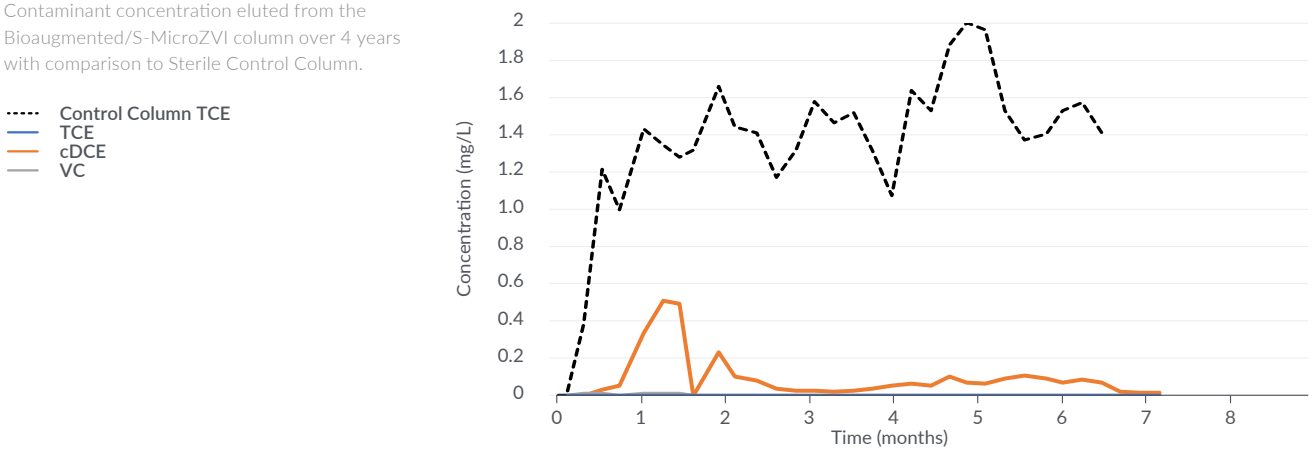


## Bioaugmented/S-MicroZVI Column

The performance of the bioaugmented/S-MicroZVI column over 7 months is shown in Figure 4. Over the entire duration of the study the eluted TCE concentrations were non-detectible at the resolution limit of 5 ng/L. In the early stages of the column study (<2 months) cDCE eluted at concentrations as high as about 0.5 mg/L or about 30% of the TCE influent on a molar basis. After 2 pore volumes the column equilibrated with cDCE concentration about 1-5% molar percent relative to the TCE influent with no vinyl chloride. At the conclusion of the soil column experiment, the column was extracted, and no chlorinated compounds were detected.

**Figure 4** **Bioaugmented/S-MicroZVI Column**

Contaminant concentration eluted from the Bioaugmented/S-MicroZVI column over 4 years with comparison to Sterile Control Column.



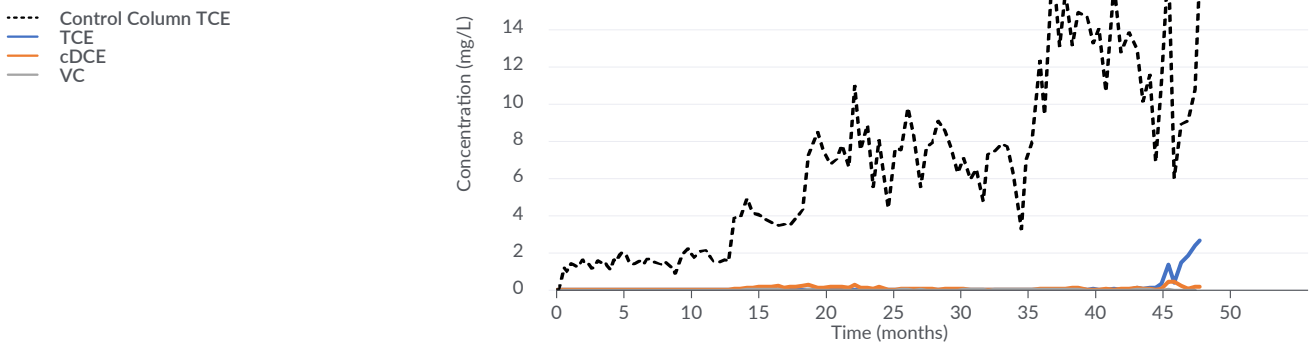

## S-MicroZVI Column

The effluent concentration data from the S-MicroZVI column are depicted in Figure 5. The concentration of TCE, cDCE, and VC in the S-MicroZVI column were below or near the detection limit for the first 12 months. Subsequently, the influent was increased to 5 mg/L TCE and switched from anoxic to 50% DO saturation to increase the electron acceptor flux and create a more demanding environment. The increased flux had little effect on TCE elution which remained at or near detection limit. The concentration of cDCE eluting from the system in this environment increased to about 0.2 mg/L cDCE corresponding to a molar reduction of at least 95%. This result is consistent with in-house laboratory studies and published work showing that the beta-elimination pathway is the primary degradation route for the chemical reduction of TCE Figure 1.

## Figure 5

## S-MicroZVI Column

Contaminant concentration eluted from S-MicroZVI column over 4 years with comparison to Sterile Control Column.




At 19 months, the TCE concentration of the influent was increased to 10 mg/L TCE at 50% DO saturation. Doubling the TCE concentrations had little effect on the effluent concentrations which were similar to those measured when influent concentrations were 5 mg/L TCE. At 24 months, the influent was changed to 10 mg/L TCE and 100% DO saturation. This had no adverse effect on column performance, with steady to slightly lower cDCE elution. At 36 months, influent concentration of TCE was increased to 20 mg/L and 100% DO saturation. The system operated under these conditions for an additional 12 months. TCE and cDCE effluent concentrations were stable until month 45 at which time moderately higher breakthrough concentrations of TCE and cDCE were observed. The 4-year run of the long-term S-MicroZVI columns ended with a breakthrough of 2.7 mg/L TCE and 0.47 mg/L cDCE from a 20 mg/L and 100% DO saturation influent equating to a greater than 80% contaminant elimination. At the conclusion of the soil column experiment, the column was extracted, cDCE on soil was 0.02 mg/kg or less, and TCE on soil was 0.25 mg/kg or less. The absence of residual TCE or daughter products further suggests TCE was being fully transformed over the course of the 4 year study.

# Conclusion

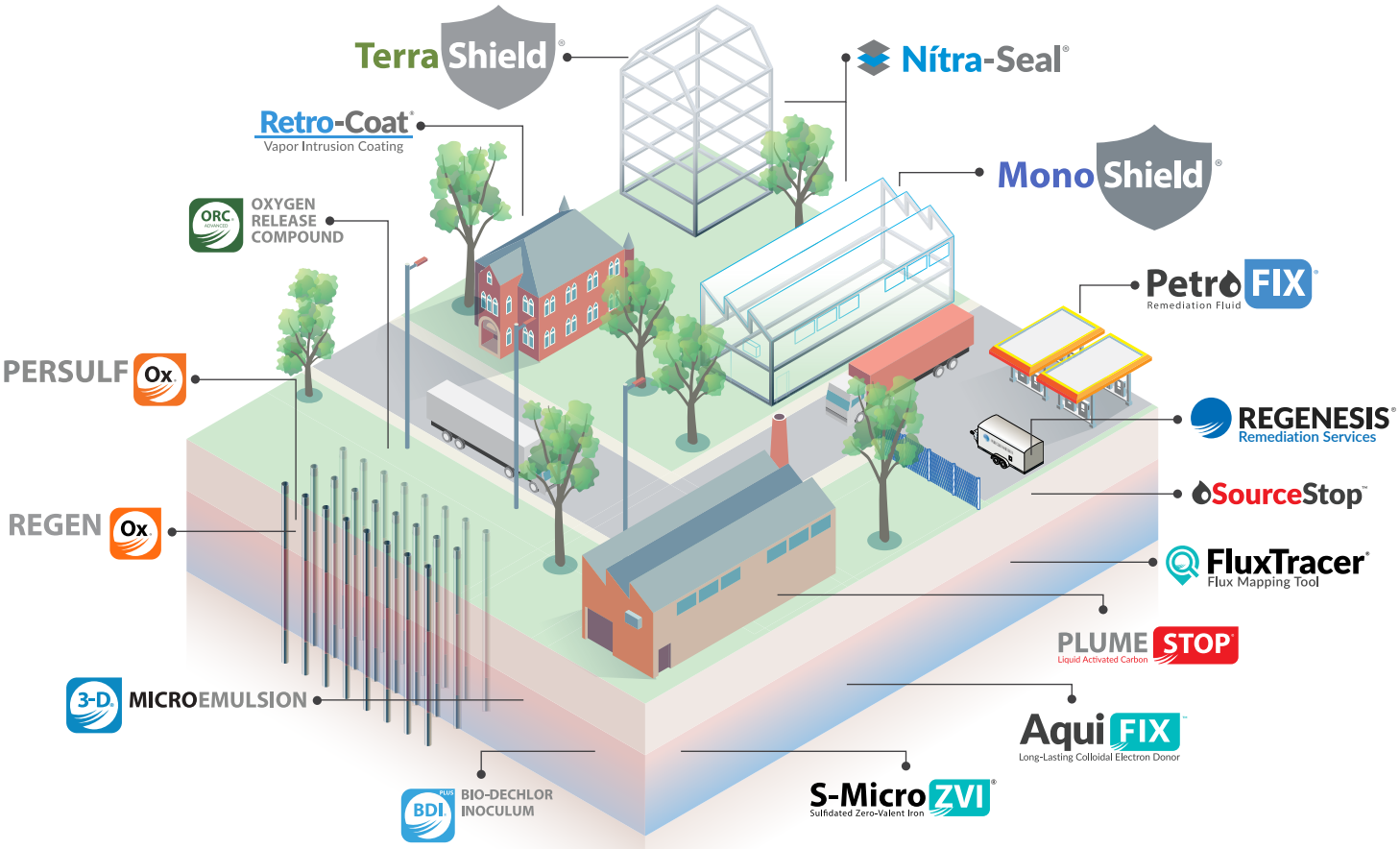
This study exhibited the ability of S-MicroZVI to degrade chlorinated solvents over almost 4 years while substantially limiting the formation of the toxic daughter products cDCE and VC under increasingly demanding conditions. S-MicroZVI promotes direct chemical reduction and assists biodegradation processes that eliminate dissolved phase chlorinated ethenes in an environment simulating a permeable reactive barrier. Product persistence is further enhanced by the sulfidation of the particle surface which inhibits the unwanted hydrolysis reaction between ZVI and water. Overall, S-MicroZVI is an effective product that works efficiently to degrade chlorinated ethenes and daughter products.

## References:


1. *Fan, D., O'Brien Johnson, G., Tratnyek, P. G., & Johnson, R. L. (2016). Sulfidation of Nano Zerovalent Iron (nZVI) for Improved Selectivity During In-Situ Chemical Reduction (ISCR). Environ. Sci. Technol. 50, 9558–9565 (2016).*

2. *ISCR-Enhanced Bioremediation. (n.d.). Retrieved March 24, 2023, from https://REGENESIS.com/wp-content/uploads/2019/02/ISCR-Tech-Bulletin-2-column-1.11.19-For-Web-1.pdf*

3. *Zero-Valent Iron Technical Bulletin. (n.d.). Retrieved March 24, 2023, from https://REGENESIS.com/wp-content/uploads/2019/02/Sulfidation-Tech-Bulletin-2-column-layout_new.pdf*




## About REGENESIS

At REGENESIS we value innovation, technology, expertise and people which together form the unique framework we operate in as an organization. We see innovation and technology as inseparably linked with one being born out of the other.

Inherently, innovation imparts new and better ways of thinking and doing. For us this means delivering expert environmental solutions in the form of the most advanced and effective technologies and services available today.

We value expertise, both our customers' and our own. We find that when our experienced staff collaborates directly with customers on complex problems there is a high potential for success including savings in time, resources and cost.

At REGENESIS we are driven by a strong sense of responsibility to the people charged with managing the complex environmental problems we encounter and to the people involved in developing and implementing our technology-based solutions. We are committed to investing in lasting relationships by taking time to understand the people we work with and their circumstances. We believe this is a key factor in achieving successful project outcomes.

We believe that by acting under this set of values, we can work with our customers to achieve a cleaner, healthier, and more prosperous world.

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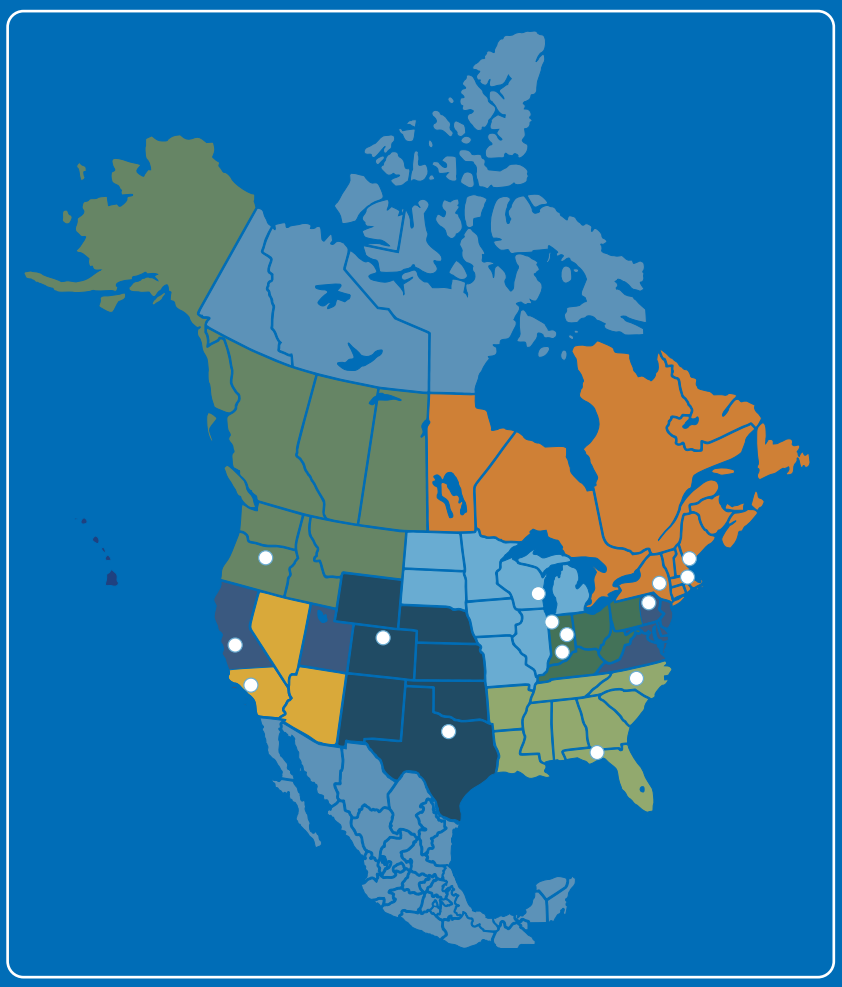

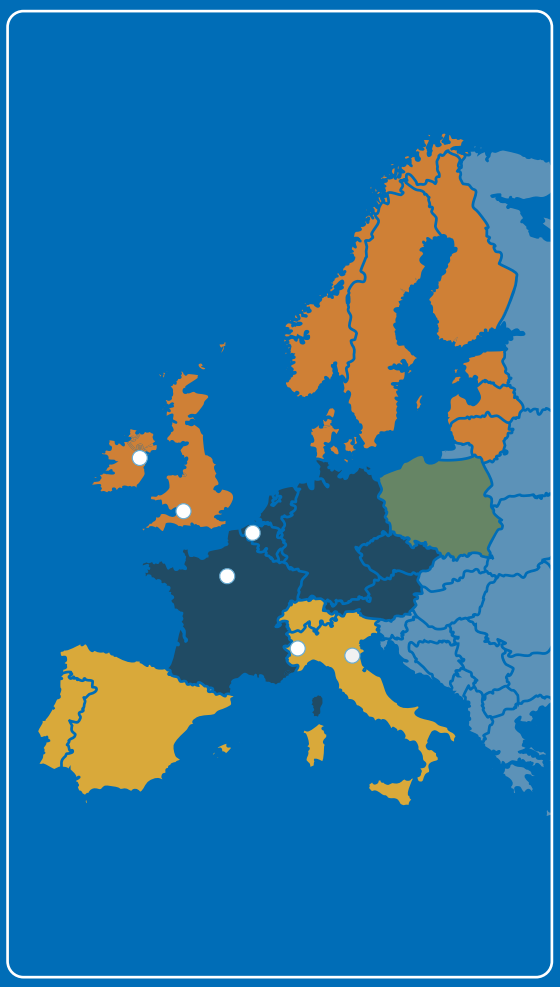


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